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Purification of Silicontetraiodide by Zone-refining Process

By Hideo BABA, Tadashi NOZAKI and Hidemaro ARAKI

(Received July 12, 1958)

In spite of the superior properties of silicon as a semiconductor material, the electronic devices such as silicon transistors or power rectifiers have not been fully developed. One of the causes of this comes from the fact that the techniques of purification of this material are more difficult than those of germanium. The refining process of silicon would have to choose another direction from that of germanium especially in its chemical purification steps. Moreover, elementary silicon is so chemically active in its molten state that the zone refining can not be carried out in the same way as in the case of germanium. For these reasons, chemical purification is important to obtain a highly pure silicon.

Several methods have been presented for obtaining transistor grade silicon[1-4], but among them, the so called du Pont method is the most predominant in the industrial aspect at present. On the other hand, we expect that the silicon iodide method will be one of the promising ones for improving the purification processes. First of all, the most important problem is the methods of removing impurities in silicontetraiodide. Of course, the usual refining processes such as recrystallization, distillation and sublimation are also applicable in this case, but in addition to them, the zone-refining process, which has been proved excellent for the purification of germanium[5], may be applied to this compound. But the behavior of impurity elements in the iodide during this process has not been made clear. As some elements such as boron, phosphorus and arsenic are removed with difficulty by the zone-refining of elementary silicon[6], it is preferable to remove them from it beforehand. For this reason, we studied the behavior of a trace of boron and phosphorus in silicontetraiodide during the normal freezing and zone-melting of the material.

Recently, Rubin et al. studied the zone-melting of silicontetraiodide and they determined the segregation coefficients of several elements by spectrographic analysis[7]. But as they pointed out, the concentrations of impurities at the top of the charge were too far below the limits of spectrographic detection for some elements to make clear the details of the impurity distribution through the charge.

Experimental Results

Behavior of Phosphorus in Silicontetraiodide.—*a) Preparation of radioactive phosphorusiodide.*—Radio isotope ^{32}P is conveniently used to trace the behavior of phosphorus during the zone melting process of silicontetraiodide. Phosphorus in silicontetraiodide will not be present in its elemental state but will exist as some iodine compounds such as diphosphorus tetraiodide or phosphorus triiodide. Radio isotope ^{32}P can easily be produced by deuteron radiation. But neither kind of phosphorus, red or yellow, can be irradiated in the cyclotron because of its high vapor pressure. In order to avoid these difficulties, it is preferable to use some phosphorus alloy. Pure copper foil with 99.96% purity and 0.2 mm. thick was vacuum-sealed with red phosphorus in a quartz tube, and was heated at 300°C for about ten hours in a furnace. During this heat treatment, the phosphorus diffused into copper and the surface of the foil turned silver white in color. This alloy was irradiated by deuteron in cyclotron to make it radioactive.

The thus activated Cu—P alloy was treated with toluene containing iodine at its boiling point for about two hours to dissolve out the activated phosphorus, and labeled phosphorusiodide could be obtained. A little portion of activated copper was accompanied with phosphorusiodide in solution forming copper iodide, but the influence of γ rays emitted from ^{64}Cu could be neglected in measuring β rays emitted from ^{32}P using a Geiger counter. Toluene solution containing radioactive phosphorusiodide was added to crystalline siliconiodide and it was dissolved completely by the addition of boiling toluene. Then it was cooled at 0°C for several hours to crystallize out

1) H. V. Wartenberg, *Z. Anorg. allgem. Chem.*, **265**, 186 (1951).
2) D. W. Lyon, C. M. Olsen and E. D. Lews, *J. Elect. Chem. Soc.*, **96**, 359 (1949).
3) H. C. Theuerer, *Bell Tel. Lab. Rec.*, **33**, 327 (1955).
4) F. B. Litton and H. C. Anderson, *J. Elect. Chem. Soc.*, **101**, 287 (1954).
5) W. Pfann, *J. Metals*, **194**, 747 (1952).
6) J. A. Burton, *Physica*, **20**, 845 (1954).
7) B. Rubin, G. H. Moates and J. R. Weiner, *J. Elect. Chem. Soc.*, **104**, 656 (1957).

the silicon iodide contaminated with radioactive phosphorus.

b) Measurement of phosphorus distribution by the radiochemical method. — Segregation Experiments. — The thus prepared silicon iodide was sealed in a quartz tube of 15 mm. diameter and 30 cm. length under reduced pressure. The content was melted by heating uniformly and cooled rapidly so that no segregation of the impurity would occur and was followed by the measurement of the initial distribution of ^{32}P. As shown in Fig. 1, the tracer was distributed uniformly throughout the rod. The content was melted again completely in a furnace which was long enough to melt it uniformly, then the quartz tube was moved down with a speed of 2.2 mm. per minute. The melted silicon iodide was solidified from the top portion outside of the furnace gradually. As a little part of the silicontetraiodide was hydrolyzed by atmospheric moisture, the melted portion of silicon iodide became somewhat turbid. But hydrolyzed products were easily segregated and transferred toward the upper part of the rod.

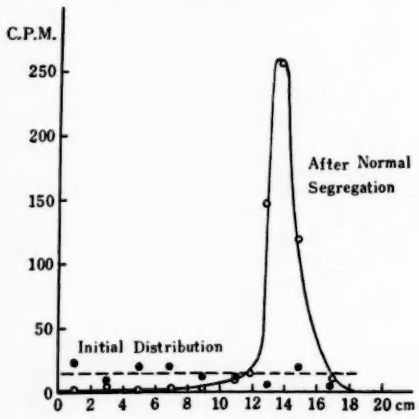

Fig. 1. Distribution of phosphorus after normal freezing.

The distribution of phosphorus after normal segregation could be found by measuring the radioactivity of β-rays emitted from ^{32}P at every 10 mm. length of the rod using a sealing device. The results are shown by curve 2 in Fig. 1 by plotting the counting rate against the distances from the top of the rod.

This method was convenient to carry out the experiment of segregation or zone melting processes, because repetition using the same sample was possible. But the selfabsorption by silicontetraiodide and the absorption by quartz wall made the counting rate less, and when the iodide changed its phase, liquid to solid and vice versa, local strong strength sometimes broke the quartz tube.

These troubles could be avoided by using a quartz boat instead of a tube as shown in Fig. 2.

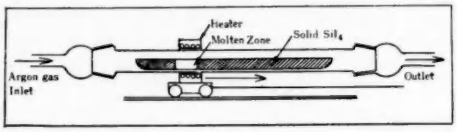

Fig. 2. Zone melting of silicontetraiodide.

2. In this case, dried argon gas was introduced gently from the top of the boat to carry the evaporated iodide toward the end of the boat. After normal segregation or zone refining processes, the rod of silicon iodide was taken off from the boat and cut into about ten segments, and each

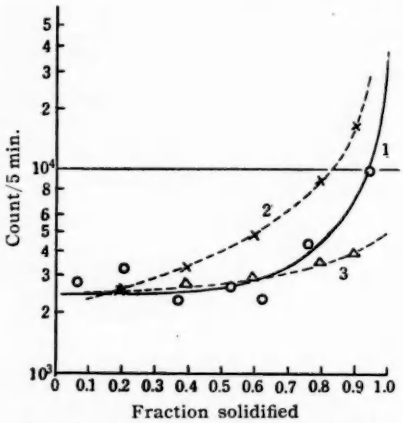

Fig. 3. Distribution of phosphorus in silicontetraiodide after normal segregation.
1. Experimental Result
2. Calculated $k=0.1$
3. 〃 $k=0.8$

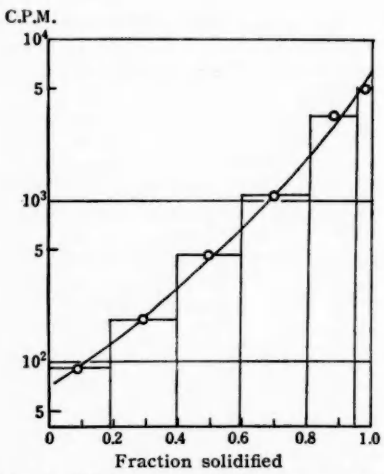

Fig. 4. Distribution of phosphorus after three passes of molten zone.

of them was weighed quickly avoiding the hydrolysis by the atmospheric moisture. Then they were hydrolyzed in a quartz evaporating dish by adding distilled water and dried up on a hot plate. The radioactivity of the samples thus obtained was measured by a Geiger counter.

The results are shown in Fig. 3. Curve 1 indicates the distribution of phosphorus after normal segregation with a velocity of 2.5 mm./min., and Fig. 4 shows the result of zone refining of three passes with a velocity of 0.83 mm./min. In both cases the counts of one gram of hydrolyzed products per five minutes were plotted against a solidified fraction of the iodide bar.

Behavior of Boron in Silicontetraiodide.—*Determination of boron by colorimetric method using curcumin.*—As it is impossible to trace the behavior of boron by using its radioisotope because of its short half life, there is no way but chemical analysis for this purpose. The colorimetric method using curcumin seemed to be the most satisfactory.

Several reports have been published on the determination of boron by this method[8-11]. But some of them have poor reproducibility, because coloring conditions, such as the concentration of the reagents, the time of treating, the evaporation temperature and the dissolving method of formed curcumin-boron complex, affect the results significantly.

Reagents.—*a*) *Curcumin-oxalic acid solution.*—Dissolve 5.0 mg. of crystalline curcumin and 0.5 g. of recrystallized oxalic acid in 50 ml. of redistilled ethanol. This solution was prepared freshly immediately before use and kept cold.

b) *Boron standard solution.*—Dissolve 0.1430 g. of boric acid (extra pure grade) in 500 ml. of redistilled water. Dilute 5.0 ml. portion of this stock solution to 500 ml. (the boron content will be 0.5 γ per ml.).

Standard Reference Curves.—Taking zero to 5.0 ml. of the standard boron solution in quartz evaporating dishes, 1 ml. of hydrochloric acid (1 : 1) and 2 ml. of curcumin oxalic acid solution were added, then they were diluted with distilled water to make the total volume 8 ml. These evaporating dishes were floated on a water bath which was kept at 55±2°C until the contents were dried up. The evaporation could be accelerated by the aid of a gentle air flow on the liquid surface. Ten ml. of ethanol was added to each dish to dissolve the residue, and the solution was transferred to an absorption measurement cell of 10 mm. length. The absorbancy at 540 mμ was measured using a spectrophotometer.

As shown in Fig. 5, curcumin solution itself has absorption maximum at 430 mμ, while boron complex has its maximum at 540 mμ. The curcumin-boron complex is rather stable and no detectable change was observed after several hours as shown in this figure. Beer's law plot is shown in Fig. 6. It was necessary to make

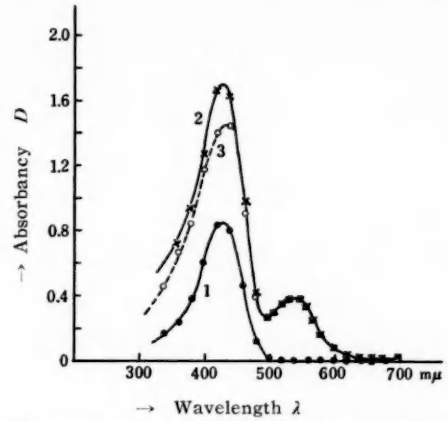

Fig. 5. Light absorption curves of curcumin-oxalic acid solution and curcumin-boron complex.
1. Curcumin solution
2. Curcumin-boron complex (initial absorption)
3. Curcumin-boron complex (after 17 hr.)

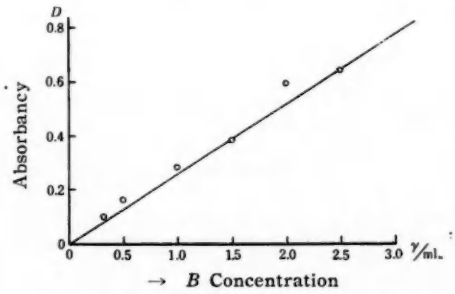

Fig. 6. Beer's law plot of curcumin-boron complex.

blank tests on each sample in order to minimanize the fluctuation of the results.

Determination of Born Distribution in Zonerefined Silicontetraiodide.—Generally, elementary silicon used for iodination experiment contains enough boron in itself, so that a detectable amount of boron should be present in iodide without adding any on purpose. So the hydrolyzed product used for activity measurement of ^{32}P could be used for the determination of boron. About 10 ml. of distilled water was added to the sample and it was heated gently in a quartz evaporating dish to extract the boron into solution as boric acid. Then it was filtered and the precipitate of silicon dioxide on filter paper was washed several times with warm water to remove the boron compound completely. The filtrate was evaporated by heating in a quartz evaporating dish to about 5 ml. Using this solution, boron was determined as described above.

Curve 1 in Fig. 7 shows the distribution of

8) C. C. Luke, *Anal. Chem.*, **27**, 1150 (1955).
9) W. T. Dible, E. Truog and K. C. Berger, ibid., **26**, 418 (1954).
10) H. Kramer, ibid., **27**, 144 (1955).
11) J. H. Yoe and R. L. Grob, ibid., **26**, 1465 (1954).

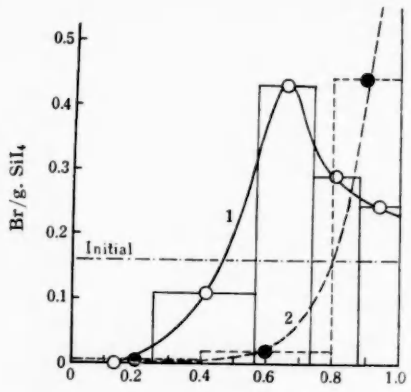

Fig. 7. Distribution of boron after zone refining with different moving speed.
1. Six passes (2.4 mm./min.)
2. Three passes (0.83 mm./min.)

boron after six passes of single zone with a moving speed of 2.4 mm. per min., and curve 2 shows that of three passes with a speed of 0.83 mm./min. In both cases the width of the molten zone was about 20 mm.

Consideration of the Results

Several studies have been reported on the segregation effect of the binary solution of metals. The zone purification method was developed from this principle by Pfann, and the behavior of impurity elements in semiconducting materials has been made clear by many workers. It is well known that the distribution of impurity concentration throughout the ingot after normal segregation is expressed by the equation[5]

$$C = kC_0(1-g)^{k-1} \qquad (1)$$

In this equation, g represents the solidified fraction, C_0 the initial concentration, C the impurity concentration at a point g, and k the distribution constant defined by the ratio of impurity concentration in solid to that in liquid. In the case of segregation of phosphorus in silicontetraiodide this equation may be also applicable. Let k be equal to 0.1 and 0.8, the distributions of phosphorus throughout the iodide bar are represented by curve 2 and 3 respectively in Fig. 3. Comparing these curves with experimental results, it can be said that the results can not be represented by the above equation, but it consists of two different k values. As colloidal silicon dioxide produced by the hydrolysis of tetraiodide has a tendency to adsorb phosphorus as well as some other trace impurities, it is reasonable to consider that a part of phosphorus will be adsorbed by the colloidal silicon dioxide and segregated together. For the reason given above, the beginning portion of the curve shows a large k value corresponding to the distribution constant of phosphorus itself, and the end portion of the curve shows a small k value which corresponds to that of the hydrolyzed product. In this case, the segregation equation can be written as

$$C = C_0\{k_1(1-g)^{k_1-1} + k_2(1-g)^{k_2-1}\} \qquad (2)$$

Curve 1 and 2 in Fig. 8 show the distribution of solute assuming $k=0.1$ and $k=0.8$ respectively. Curve 3 shows the result of calculation from Eq. 2 using $k_1=0.1$ and $k_2=0.8$. C_0 is unity in each case. The resultant curve 3 shows good correspondence with experimental results.

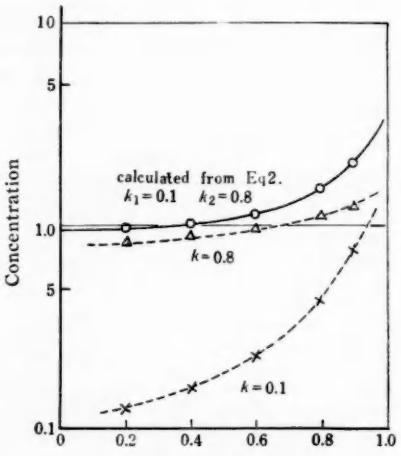

Fig. 8. Resultant distribution calculated from Eq. 2. $k_1=0.1$ $k_2=0.8$

The results of the zone refining process showed a promising effect to remove phosphorus after three passes of single zone, for instance, the concentration could be decreased one tenth of the initial amount at the top portion and the ratio of concentration of phosphorus at the end and the top parts of the bar reached three powers of ten.

As for boron, the results were not so distinct as in the cace of phosphorus, but better refining efficiency could be expected by this process than in the case of its elementary state.

Summary

The behavior of phosphorus and boron as impurity elements in silicon tetraiodide was studied during the normal segregation and zone melting processes. Both of them can be removed efficiently by this process, and it is considered that the colloidal hydrolyzed product suspended in silicon tetraiodide plays a predominant role for segregation because of its high adsorptivity to these elements. The distribution curve of radioactive phosphorus seems to show the influence of this material.

The authors are pleased to express their gratitude to the Director Dr. T. Niimi, and Dr. S. Yanagisawa, Professor of Chemistry at Keio University, for helpful guidance and encouragement during the course of this study.

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Formation of Tetraazaporphin from Phthalic Anhydride and its Reduced Products

By Masahiro SHIGEMITSU

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Phthalic anhydride easily reacts with urea and metallic salts to produce metal phthalocyanine, a kind of tetraazaporphin. Particularly, copper phthalocyanine which is obtained almost quantitatively by the above reaction is one of the most widely used blue organic pigments. But in the case of 3, 4, 5, 6-tetrahydrophthalic anhydride which is the reduced product of phthalic anhydride, the yield of tetraazaporphin is rather small[1].

In the present experiment, the effect of structure of the starting materials on the tetra-azaporphin formation was examined. Phthalic anhydride (I), 3,4,5,6-tetrahydrophthalic anhydride (II), 1,2,3,6-tetrahydro-*cis*-phthalic anhydride (III), hexahydro-*cis*-phthalic anhydride (IV) and 3,6-endomethylene-1,2,3,6-tetrahydro-*cis*-phthalic anhydride (V) were chosen as the examples for the starting materials.

Experimental

Materials.—Phthalic anhydride (I), m. p. 130～131°C. 3,4,5,6-Tetrahydrophthalic anhydride (II) was prepared by reducing phthalic anhydride with sodium-amalgam, m. p. 68～69°C (reported m.p. 68～69°C)[2] (*Anal.* Found: C, 63.09; H, 5.20. Calcd. for $C_8H_8O_3$: C, 63.15; H, 5.26%). 1,2,3,6-Tetrahydro-*cis*-phthalic anhydride (III) was prepared with the aid of Diels-Alder reaction from butadiene and maleic anhydride, m.p. 99～101°C (reported m. p. 99～101°C)[3] (*Anal.* Found: C, 63.08; H, 5.22. Calcd. for $C_8H_8O_3$: C, 63.15; H, 5.26%). Hexahydro-*cis*-phthalic anhydride (IV) was prepared by reducing III with sodium-amalgam, m. p. 33～34°C (reported m. p. 32～33°C)[4] (*Anal.* Found: C, 62.29; H, 6.45. Calcd. for $C_8H_{10}O_3$: C, 62.34; H, 6.49%). 3,6-Endomethylene-1,2,3,6-tetrahydro-*cis*-phthalic anhydride (V) was prepared with the aid of Diels-Alder reaction from cyclopentadiene and maleic anhydride, m. p. 164～165°C (reported m. p. 164～165°C)[5,6] (*Anal.* Found: C, 65.77; H, 4.91. Calcd. for $C_9H_8O_3$; C, 65.84; H, 4.87%).

Methods.—A mixture of 15 g. of phthalic anhydride or its reduced products, cuprous chloride (1/4 mol. of starting materials as shown in Table I), 60 g. of urea, 0.5 g. of ammonium molybdate and 175 g. of nitrobenzene was heated with stirring. Tow model cases will be shown in relation to the experimental conditions. First, the mixture was stirred at room temperature for 30 min., and then heated up to 150°C during ca. 1 hr. at a definite rate, and finally at 150～155°C for 4 hr. In the second example, the mixture was stirred at room temperature for 30 min., and then heated up to 190°C during ca. 2 hr. at a definite rate, and finally at 190～195°C for 3 hr. After the reaction was completed, nitrobenzene was removed by steam distillation

1) G. E. Ficken and R. P. Linstead, *J. Chem. Soc.*, **1952**, 4846.
2) A. von Bayer, *Ann.*, **258**, 199 (1890).
3) L. F. Fieser and E. C. Novells, *J. Am. Chem. Soc.*, **64**, 806 (1942).
4) A. von Bayer, *Ann.*, **258**, 219 (1890).
5) D. Craig, *J. Am. Chem. Soc.*, **73**, 4889 (1951).
6) U. S. Pat. 2,424,948 (1947).

TABLE I. THE CONDITIONS OF REACTION AND THE YIELD OF COLORING MATTERS

Expt.	Starting material (g.)	CuCl (g.)	Temp. (°C)	Rect. prod. color	Rect. prod. wt. (g.)	Coloring matter color	Coloring matter wt. (g.)	Coloring matter yield (%)
1	I, 15.0	2.5	150~155	blue	11.3	blue	11.1	76.0
2	〃 〃	〃	190~195	〃	13.4	〃	13.1	90.5
3	II, 15.0	2.4	150~155	dark brown	9.8	violet blue	0.6	4.1
4	〃 〃	〃	190~195	〃	10.2	〃	0.2	1.4
5	III, 15.0	2.4	150~155	dark brown	11.7	—	—	—
6	〃 〃	〃	190~195	〃	10.6	—	—	—
7	IV, 15.0	2.4	150~155	dark brown	12.4	—	—	—
8	〃 〃	〃	190~195	〃	10.9	—	—	—
9	V, 15.0	2.3	150~155	dark brown	11.2	—	—	—
10	〃 〃	〃	190~195	〃	10.7	—	—	—

and the resulting mixture was heated with 5% hydrochloric acid and then 2% caustic soda, filtered, washed with water and dried at 60~70°C.

When I was used as the starting material, the coloring matter (copper phthalocyanine) was treated with ethanol to remove impurities. In the case of II, the coloring matter (copper tetracyclohexenotetraazaporphin) was extracted from the dark brown product with *o*-dichlorobenzene[7]. In the case of III, IV and V, the coloring matters (tetraazaporphins) could not be obtained by the extraction from the dark brown products with *α*-chloronaphthalene (good solvent of tetraazaporphins) and *o*-dichlorobenzene.

Coloring matters were formed only in the cases of I and II, both of which were of similar blue shades. Reflectance curves concerning these shades of colors were measured with a recording spectrophotometer (General Electric Co.). Samples were prepared in the following way. One part of copper phthalocyanine obtained from I was dissolved in 3 parts of 98% sulfuric acid at room temperature, and was poured into water. Fine crystals deposited were washed with water free from acid and dried at 60~70°C. One part of *β*-form copper phthalocyanine here obtained[8] and copper tetracyclohexenotetraazaporphin obtained from II were mixed respectively with 1.5 parts of polymerized linseed oil and were made into paste by grinding 400 rounds in Hoover automatic muller. To 1 part of this paste was added 70 parts of zinc white paste (obtained by grinding 2 parts of zinc oxide in 1.5 parts of polymerized linseed oil), which was applied in 0.5 mm. thickness on a coated paper with a bladeoapplicator (Gardner Laboratory). These were dried at room temperature and used as samples for measuring reflectance curves.

Results and Discussion

Table I shows the relation between the reaction conditions and the reaction products.

As is seen from Experiments 1 and 2 (Table I), the reaction proceeded easily at a reaction temperature of either 150~155°C or 190~195°C when the reaction was conducted with I as the starting material, copper phthalocyanine being obtained in good yield (*Anal.* Found: C, 66.78; H, 2.90; N, 19.38; Cu, 11.00. Calcd. for $C_{32}H_{16}N_8Cu$: C, 66.72; H, 2.78; N, 19.46; Cu, 11.04%). As is shown by Experiments 3 and 4, the use of II as starting material remarkably reduced the yield of the coloring matter (4.1 and 1.4%, respectively). The coloring matter obtained was copper tetracyclohexenotetraazaporphin (*Anal.* Found: C, 65.02; H, 5.54; N, 18.76; Cu,

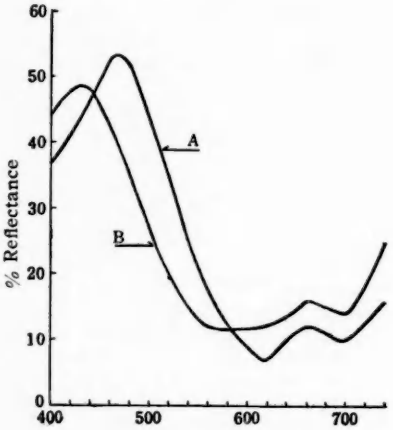

Fig. 1. Reflectance curves of *β*-form copper phthalocyanine (A) and copper tetracyclohexenotetraazaporphin (B).

7) British Pat., 686,395 (1953).
8) G. von Susich, *Anal. Chem.*, **22**, 425 (1950).

10.67. Calcd. for $C_{32}H_{32}N_8Cu$; C, 64.91; H, 5.41; N, 18.93; Cu, 10.76%).

While copper phthalocyanine slightly dissolves only in α-chloronaphthalene, copper tetracyclohexenotetraazaporphin easily dissolves in *o*-dichlorobenzene and has a color somewhat more reddish than copper phthalocyanine. Their reflectance curves are shown in Fig. 1 and their C. I. E. Notations are given in Table II. In this table, Y denotes luminosity, P_e purity and λ_D dominant wavelength.

TABLE II. C. I. E. NOTATIONS

Sample	Y%	P_e%	λ_D mμ
A	19.10	55.8	475.8
B	17.00	47.0	470.2

A; Copper phthalocyanine (β-form).
B; Copper tetracyclohexenotetraazaporphin.

The dominant wavelength of copper tetracyclohexenotetraazaporphin is shorter by 5.6 mμ than that of β-form copper phthalocyanine with blue color tinged with red.

In the Experiments 5 and 6 where III, which carries the bond in a different position from that in II, was used as starting material; only alkali-soluble dark brown products were obtained, but coloring matters could not be isolated either by α-chloronaphthalene or *o*-dichlorobenzene.

When IV (Experiments 7 and 8) which has no double bond, and V (Experiments 9 and 10) were used as starting materials, only alkali-soluble dark brown products were obtained without formation of tetraazaporphin. Thus, it was confirmed that, when I is reduced and aromaticity is weakened, or when aromaticity is very small as in the case of V, tetraazaporphin can not be produced. However, when the double bond between carbonyl groups is not reduced, tetraazaporphin is produced, though the yield is small.

In Experiments 1 and 2, higher reaction temperature increased the yield of the coloring matter, but, on the contrary, the increase in the temperature decreased the yield in the Experiments 3 and 4. This may be due to the decomposition of II which on heating over approximately 200°C, gives up carbon dioxide and converts into resinous material of m. p. 50~55°C. Fig. 2 shows infrared spectrum of II and Fig. 3 that of its product obtained by heating. These spectra (in potassium bromide pellet) were obtained with Perkin Elmer 12B instrument.

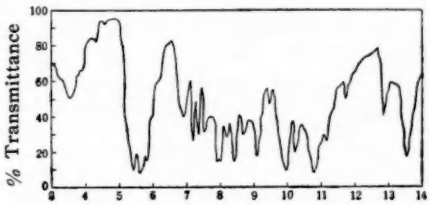

Fig. 2. Infrared spectrum of 3,4,5,6-tetrahydrophthalic anhydride (KBr).

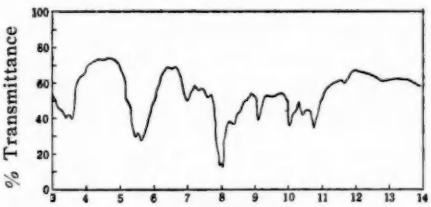

Fig. 3. Infrared spectrum of the product obtained by heating 3,4,5,6-tetrahydrophthalic anhydride (KBr).

In the reaction of II, higher reaction temperature seemed to decrease the yield of the coloring matter and accelerate the conversion into resinous material.

The author gratefully acknowledges the instruction of Dr. Ryozo Goto, Professor of Kyoto University; also Dr. Takahisa Nakamura and Dr. Wataru Ishikawa, Toyo Ink Mfg. Co. The author's thanks are also due to Mr. Ryuichi Kimura, Kyoto University, in measuring the infrared spectra.

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Reduction of Copper Hexadecachlorophthalocyanine

By Masahiro SHIGEMITSU

(Received September 25, 1958)

It was manifest by the previous study[1] that the darkening of chlorinated copper phthalocyanine green by reducing agents was caused, not by variation in forms, but by variation in its crystal structure or in its chemical composition. The degree of discoloration corresponded, though very little, to that of decrease in chlorine content, from which it was inferred that hydrogen atoms had been introduced into phthalocyanine nucleus. If phthalocyanine nucleus is to be reduced, either C=C or C=N bond is considered to be the position of reduction. Whether the position attacked is C=C or C=N is made clear by using the exhaustively chlorinated compound (copper hexadecachlorophthalocyanine, I). Hence the author used I as a sample and studied the mechanism of reduction.

Experimental

Materials. — *Copper hexadecachlorophthalocyanine (I).*—The compound which was synthesized according to the method previously reported[2], was used as chlorinated copper phthalocyanine green. Reducing agent was made to act upon it, which was then oxidized, reprecipitated and heated as follows.

Pulverization.—I was dissolved in chlorosulfonic acid, poured into ice water, and deposited as fine particles. The chlorine content was 50.33% (Calcd. 50.34%) as previously indicated[2].

Reduction.—One gram of I and 30 cc. of 20% aqueous solution of rongalit (addition compound of formalin and sodium hydrosulfite) were placed in a stainless steel autoclave of 50 cc. capacity and heated at 150~155°C for 20 min. The product was filtered off, washed with water and dried. It was dark green particles.

Oxidation of the reduced product.—One gram of the reduced product was added to 80 cc. of 2% sulfuric acid containg 0.2 g. of ceric sulfate and heated at 70~80°C for 1 hr.

Reprecipitation of the reduced product.—One gram of the reduced product was dissolved in 30 g. of chlorosulfonic acid at room temperature and poured into ice water. The precipitate thus obtained was filtered and washed with water.

Heating of the reduced product.—The reduced product was heated at 250~255°C for 3 hr. in a stream of nitrogen.

Methods.—Variation in color observed in the case of reduction of I and of oxidation, reprecipitation and heating of the reduced product was studied by measuring the reflectance curves with a recording spectrophotometer (General Electric Co.). Samples for reflectance-curve measurement were made in the same procedure as previously reported[1]. X-ray diffraction patterns of I and its reduced product were obtained with a recording X-ray diffraction apparatus (Philips Co.) and variation in crystal structure was studied.

Then, elementary analysis of I and its reduced product was conducted. Also, infrared spectra (Nujol) were taken of I, its reduced product, the reoxidized reduced product and the reprecipitated reduced product, using a Perkin Elmer 12B instrument.

Results

Reflectance Curves. — Fig. 1 shows the reflectance curves of I, its reduced product

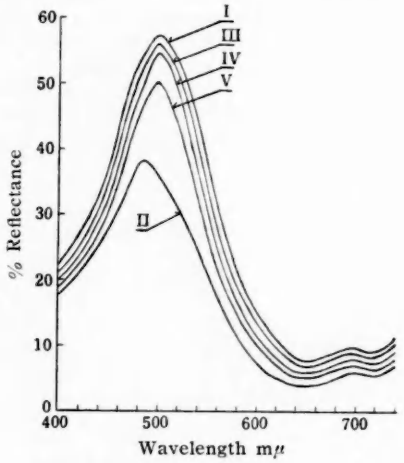

Fig. 1. Reflectance curves of copper hexadecachlorophthalocyanine (I), its reduced product (II), reoxidized reduced product (III), reprecipitated reduced product (IV) and heated reduced product (V).

1) M. Shigemitsu, This Bulletin, **32**, 502 (1959).
2) M. Shigemitsu, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **62**, 112 (1959) (presented at the Autumnal Meeting of Chemical Society of Japan, Tokyo, 1957).

(II), the reoxidized reduced product(III), the reprecipitated reduced product(IV) and the heated reduced product(V). Table I gives their C.I.E. Notations. In this table, Y denotes luminosity, P_e purity and λ_D dominant wavelength.

TABLE I. C.I.E. NOTATIONS

Sample	Y %	Pe %	λ_D mμ
I	30.34	36.8	492.6
II	22.18	39.1	488.9
III	29.96	37.2	490.8
IV	29.58	37.5	490.2
V	28.41	38.1	489.7

When a reducing agent acted upon I, its luminosity lowered from 30.34 to 22.18% and it darkened in color. When this darkened pigment was heated at 250~255°C for 3 hr. in nitrogen stream, its luminosity increased to 28.41% approaching that of untreated pigment; when being oxidized and reprecipitated, the pigment increased its luminosity to 29.96 and 29.58%, respectively, recovering color of luminosity approaching that of untreated material. Thus the variation in color is of a reversible trend.

X-ray Diffraction Patterns.—Figs. 2 and 3 show the X-ray diffraction patterns of I and its reduced product.

It was made clear by the previous study that the darkening by the action of reducing agent was not due to the change in the form of pigment particles. Now, with the aid of X-ray diffraction method, no change was observed in the crystal structure either. Thus the color change is supposed to be due to the difference in the chemical composition of the compounds in question.

Elementary Analysis.—Results of analysis of I and II are given in Table II.

TABLE II. RESULTS OF ELEMENTARY ANALYSIS

Sample	C %	H %	N %	Cl %	Cu %
I Found	34.10	0.09	9.90	50.33	5.64
I Calcd.	34.09	—	9.94	50.34	5.63
II Found	33.60	1.26	9.80	49.75	5.59
III*	33.67	1.23	9.82	49.71	5.57

*III, Calculated value when fourteen hydrogen atoms were added to I.

I contains no hydrogen, but, on reduction, its hydrogen content increased to 1.26% indicating the addition of fourteen hydrogen atoms.

Infrared Spectra.—Figs. 4, 5, 6 and 7 show infrared spectra of I, II, III and IV. Fig. 8 shows that of copper phthalocyanine containing no chlorine, which was measured by Tyler et al.[3] The lower curve in Fig. 8 denotes the use of Nujol and the upper curve, shown partly, denotes the use of hexachlorobutadiene.

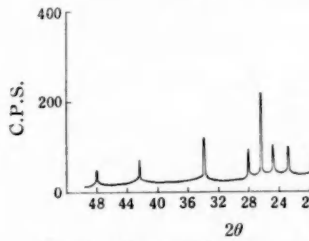

Fig. 2. X-ray diffraction pattern of copper hexadecachlorophthalocyanine (leaflet, fine particle).

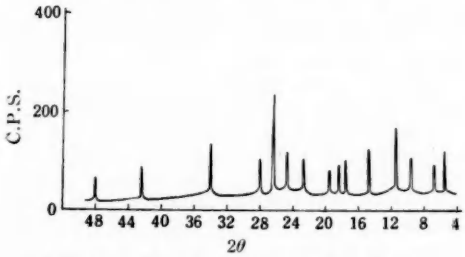

Fig. 3. X-ray diffraction pattern of reduced product of copper hexadecachlorophthalocyanine (leaflet, fine particle).

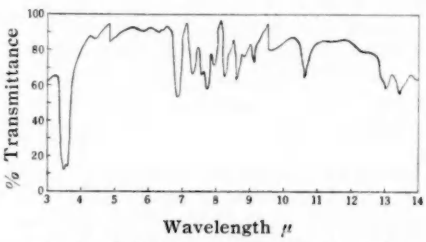

Fig. 4. Infrared spectrum of copper hexadecachlorophthalocyanine.

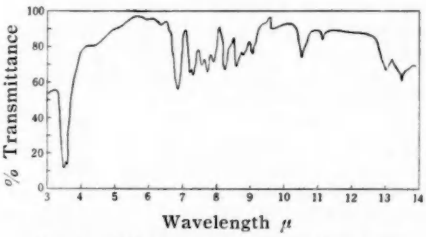

Fig. 5. Infrared spectrum of reduced product of copper hexadecachlorophthalocyanine.

3) J. E. Tyler et al., *Anal. Chem.*, **25**, 393 (1953).

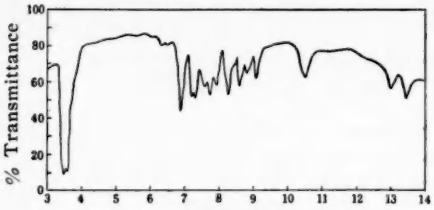

Fig. 6. Infrared spectrum of reoxidized reduced product of copper hexadecachlorophthalocyanine.

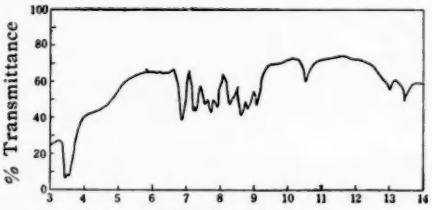

Fig. 7. Infrared spectrum of reprecipitated reduced product of copper hexadecachlorophthalocyanine.

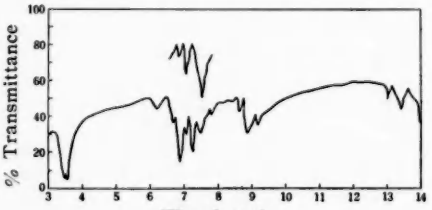

Fig. 8. Infrared spectrum of copper phthalocyanine.

When sixteen hydrogen atoms of copper phthalocyanine were chlorinated to give I, absorption bands at 720 cm^{-1}, 1090 cm^{-1}, 1125 cm^{-1}, 1290 cm^{-1} and 1415 cm^{-1} of copper phthalocyanine disappeared and those at 947 cm^{-1}, 1095 cm^{-1}, 1210 cm^{-1}, 1273 cm^{-1} and 1305 cm^{-1} were exhibited. The absorption band at 1415 cm^{-1} of copper phthalocyanine became even more conspicuous when hexachlorobutadiene was used instead of Nujol.

Discussion

Copper phthalocyanine, I and II are compared (Fig. 9). The absorption band at 1415 cm^{-1} of copper phthalocyanine disappears in I but, when being reduced, the compound shows again the absorption band at 1412 cm^{-1}. Therefore, this absorption band is due to the vibration of

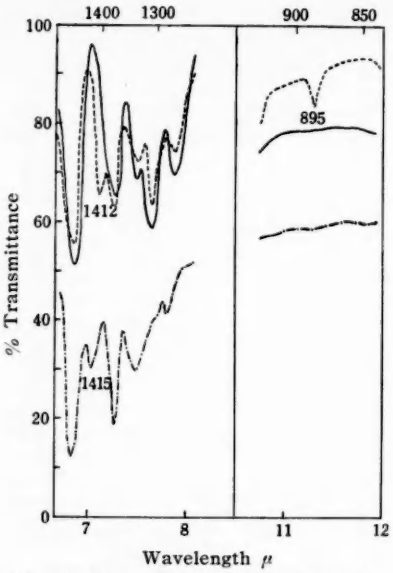

Fig. 9. Comparison of infrared spectra.
—— copper hexadecachlorophthalocyanine.
------ reduced product of copper hexadecachlorophalocyanine.
- - - copper phthalocyanine.

C–H bond of copper phthalocyanine. It is further inferred that, since C–H bending vibration appears in the range of 1475～1300 cm^{-1} [4], this absorption band may be due to the same vibration.

Further, a new absorption band appears at 895 cm^{-1} in II, but no such absorption band in I and copper phthalocyanine. Therefore, this absorption band may be attributed to the addition of hydrogen atoms. The position of the addition of hydrogen atoms is considered to be either C=C or C=N. Actually, the addition seems to proceed at C=N bond of the phthalocyanine nucleus, because the absorption band at 895 cm^{-1} corresponds to N–H bending vibration according to Colthup[4].

Gund[5] describes that cobalt phthalocyanine produces two N–H bonds when reduced. In the present experiment fourteen hydrogen atoms were added to phthalocyanine nucleus. Observing the absorption of C–H and N–H bonds which appeared in II, it is considered that twelve hydrogen atoms add to six C=C bonds and the remaining two hydrogen atoms, as inferred by Gund, produce two N–H bonds.

4) N. B. Colthup, *J. Opt. Soc. Am.*, **40**, 397 (1950).
5) F. Gund, *J. Soc. Dyers and Colourists*, **69**, 671 (1953).

Thus, the chlorination of copper phthalocyanine seems to facilitate hydrogenation at C=C and C=N bonds of phthalocyanine, and the darkening of color occurs as is observed in the reduced vat dyes.

The author gratefully acknowledges the instruction of Dr. Ryozo Goto, Professor of Kyoto University; also Dr. Takahisa Nakamura and Dr. Wataru Ishikawa, Toyo Ink Mfg. Co. The author's thanks are also due to Mr. Seiki Kato, Tokyo Institute of Technology, for his carrying out the X-ray analysis and Mr. Ryuichi Kimura, Kyoto University, for his measuring the infrared spectra.

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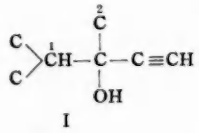
The Formic Acid Rearrangement of 3,4-Dimethyl-1-pentyn-3-ol and 3-Isopropyl-4-methyl-1-pentyn-3-ol

By Tatsuo TAKESHIMA, Ken NAGAOKA, Masataka YOKOYAMA and Shigeki MORITA

(Received November 4, 1958)

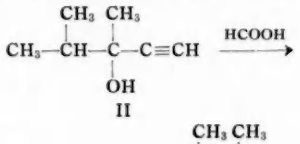
Continuing the study of Rupe reaction of ethynylcarbinols of type I[1], we now show that 3,4-dimethyl-1-pentyn-3-ol (II) and 3-isopropyl-4-methyl-1-pentyn-3-ol (III) on treatment with formic acid afford, in addition to ketone which forms the main product in each case, each corresponding aldehyde (II_b and III_b) in 5* and 6% yield respectively.



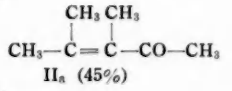
I

C[1]: Tertiary carbon atom.
C[2]: Other than secondary carbon atom.

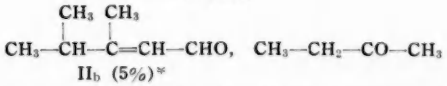
The reaction product from II was separated into three fractions. The main bulk of the low-boiling fraction (fraction 1; 45% yield) consisted of 3,4-dimethyl-3-penten-2-one (II_a)[2]. The high-boiling fraction (faction 3; 5% yield) reacted with carbonyl reagents (consult Table I) and had an unsaturated aldehydic nature. On treatment with phenylhydrazine it gave a product which had a pyrazoline reaction of a coloration different from that in the case of II_a. The hydrogenation product of this fraction also was positive toward Schiff test, the coloration being different from that of the original substance. Thus, together with analyses, 3,4-dimethyl-2-pentenal (II_b) was assigned to the compound. The facts that it is impossible for the geometrical isomer to exist for II_a and also the trend of Rupe reaction are corroborative of the structure.



II



II_a (45%)



II_b (5%)*

The intermediate fraction (fraction 2) consisted of a mixture of II_a and II_b; the quantity of the aldehyde contained diminished on standing. The forerun in the case of the distillation contained a considerable amount of methyl ethyl ketone, which owes its origin possibly to the hydrolytic fission of II_a.

The reaction product of III was distilled and three fractions were collected. The greater part of the low-boiling fraction

1) T. Takeshima, K. Wakamatsu and A. Furuhashi, This Bulletin, **31**, 640 (1958).

* The actual yield of the aldehyde seemed to be much more, considering its considerable amount contained in fraction 2.

2) H. Favre and H. Schinz, *Helv. Chim. Acta*, **35**, 2388 (1952); F. C. Whitmore et al., *J. Am. Chem. Soc.*, **63**, 643 (1941).

TABLE I. REACTION PRODUCTS FROM II

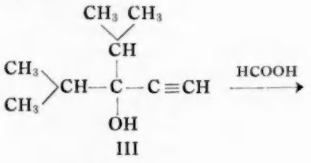
Fraction	B. p., °C	Yield, g. from 20 g. of II	Constituent
Forerun	~133	A small amount	Considerable amt. of methyl ethyl ketone
1	143~151	9	II_a
2	152~159	1.2	II_a, II_b
3	160~164	1.0	II_b

DERIVATIVES OF THE CARBONYL COMPOUNDS

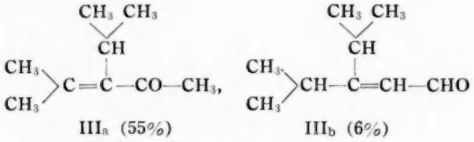
Original Compd.	2,4-Dinitrophenylhydrazone		Semicarbazone	
	M. p., °C	Appearance	M. p., °C	Appearance
II_a	132~133[3]	Lustrous orange plates or long plates	185~187[4] (slow heating) 198~199[4] (rapid heating)	Colorless plates
II_b	205~206	Red plates	163~164 (slow heating) 173~174 (rapid heating)	Colorless plates

(fraction 1; 55% yield) was considered to be 3-isopropyl-4-methyl-3-penten-2-one(III_a) reported by Hickinbottom et al.[5]; it gave no crystalline derivative with common carbonyl reagents**.

The high-boiling fraction (fraction 3; 6% yield) had an unsaturated aldehydic nature, which gave characteristic derivatives with carbonyl reagents (consult Table II). On treatment with phenylhydrazine, it yielded an oily product which had a pyrazoline reaction of a coloration different from that in the case of III_a. Viewed from these facts together with analyses and also with the course of the reaction, the compound was assigned 3-isopropyl-4-methyl-2-pentenal (III_b). Here also, the absence of geometrical isomer substantiates the structure. Young and Roberts[6] reported the 2,4-dinitrophenylhydrazone of m. p. 151.5~153°C (from ethanol) as the one of III_b without rigid isolation of the original aldehyde which was formed by ozonolysis of crotyldiisopropylcarbinol. However the 2,4-dinitrophenylhydrazone obtained in the present experiment had m. p. 173.5~174°C; its appearance (light red plates) resembled that reported[7] (bright red). Further, III_b was hydrogenated to give a saturated aldehyde which afforded a characteristic 2,4-dinitrophenylhydrazone (consult Table II) and was considered to be 3-isopropyl-4-methylpentanal (IV_b).



III



III_a (55%) III_b (6%)

The intermediate fraction (fraction 2) which was of a relatively small quantity also contained some III_b.

Experimental

3,4-Dimethyl-1-pentyn-3-ol (II).—The carbinol was prepared from methyl isopropyl ketone according to the usual manner[8]. B. p. 132~133°C.

The Formic Acid Rearrangement of II.—Twenty grams of II was gently refluxed for ca. 1 hr. with 160 g. of ca. 80% formic acid. The reaction mixture was allowed to cool and was worked up in the usual manner[1]. Fractions collected were: forerun up to 133°C, a small amount; (1) b. p. 143~151°C, 9 g., yield 45%; (2) b. p. 152~159°C, 1.2 g.; (3) b. p. 160~164°C, 1 g., yield 5%. All these fractions were colorless when freshly

3) Reported, 132~133°C. See Ref. 2.
4) Reported, 185.5~187.5°C and 194~196°C. See Ref. 2.
5) W. J. Hickinbottom, A. A. Hyatt and M. B. Sparke, *J. Chem. Soc.*, **1954**, 2529.
**Hydrogenation product of III_a which was considered to be 3-isopropyl-4-methyl-2-pentanone (IV_a), on treatment with 2,4-dinitrophenylhydrazine, gave only an oily yellow derivative, the color being apparently different from that in the case of the original ketone.
6) Wm. G. Young and J. D. Roberts, *J. Am. Chem. Soc.*, **67**, 319 (1945).
7) See Ref. 6.
8) Y. R. Naves and P. Ardizio, *Helv. Chim. Acta*, **31**, 2252 (1948).

TABLE II. REACTION PRODUCTS FROM III

Fraction	b. p., °C	Yield, g. from 20 g. of III	Constituent
1	67～71 (19 mm.)	11	III_a
2	72～80 (19 mm.)	1	III_a, III_b
3	85～91 (19 mm.)	1.2	III_b

DERIVATIVES OF THE CARBONYL COMPOUNDS

Original Compd.	2,4-Dinitrophenylhydrazone		Semicarbazone	
	M. p., °C	Appearance	M. p., °C	Appearance
III_a	—	Red oil	Could not be obtained	
IV_a	—	Yellow oil	—	—
III_b	173.5～174[6]	Light red plates	208～210	Colorless micro-needles
IV_b	86～88	Yellow plates	—	—

distilled, hardly soluble in water, had camphor-like odor, instantly decolorized bromine water, and reacted with carbonyl reagents. Fraction 1 especially turned yellowish on standing. Fraction 3 had a less camphoraceous odor and, at the same time, a somewhat stimulative smell.

The lower-boiling fractions seemed, from ammoniacal silver nitrate test, still to contain a small amount of the unreacted original carbinol.

Fraction 1 (3,4-dimethyl-3-penten-2-one, II_a) was treated with phenylhydrazine hydrochloride in ethanolic acetic acid in the usual manner of preparation of pyrazoline. A trace of the reaction mixture thus formed gave a pyrazoline reaction of brownish purple color with sulfuric acid and sodium nitrite; the color was apparently different from that in the case of fraction 3; in the latter case a deep pink-purple color was produced.

Fraction 3 (3,4-dimethyl-2-pentenal, II_b) gave positive test with Schiff reagent (pink-purple color) and reduced ammoniacal silver nitrate. On heating it turned Fehling solution into turbid bluish green[1]. That the greater part of the fraction consisted of II_b was ascertained from the quantity obtained of its 2,4-dinitrophenylhydrazone mentioned below. A considerable amount of the same derivative was also obtained from fraction 2 when the fraction was treated immediately after the distillation; the aldehyde diminished on standing, owing possibly to autoxidation and polymerization.

Fraction 3 was hydrogenated with palladium. The crude oily product was positive toward Schiff test (pink color). The amount was insufficient for rigid purification.

The forerun up to 133°C, which was of a small amount, contained a respectable quantity of methyl ethyl ketone which was obtained in the form of its 2,4-dinitrophenylhydrazone; the derivative had m. p. 116～117°C which was undepressed on admixture with an authentic specimen.

2,4-Dinitrophenylhydrazone of II_a was recrystallized from pyridine-ethanol in lustrous orange plates or long plates, m. p. 132～133°C.

Anal. Found: N, 19.26. Calcd. for $C_{13}H_{16}O_4N_4$: N, 19.17%.

Semicarbazone of II_a was recrystallized from methanol, colorless plates, m. p. 185～187°C (slow heating), 198～199°C (rapid heating).

Anal. Found: N, 24.93. Calcd. for $C_8H_{13}ON_3$: N, 24.83%.

2,4-Dinitrophenylhydrazone of II_b was recrystallized from pyridine-methanol, red plates, m. p. 205～206°C, easily soluble in hot pyridine.

Anal. Found: C, 53.27; H, 5.61; N, 19.17. Calcd. for $C_{13}H_{16}O_4N_4$: C, 53.42; H, 5.52; N, 19.17%.

Semicarbazone of II_b was recrystallized from ethanol, colorless plates, m. p. 163～164°C (slow heating), 173～174°C (rapid heating).

Anal. Found: N, 25.33. Calcd. for $C_8H_{13}ON_3$: N, 24.83%.

3-Isopropyl-4-methyl-1-pentyn-3-ol (III).—Prepared from diisopropyl ketone according to the method used in the preparation of II. B. p. 161～164°C (reported 162～164°C; prepared by the liquid ammonia method)[9]. Yield, ca. 50%.

Diisopropyl Ketone.—A mixture of 80 g. of isobutyric acid and 110 g. of lead monoxide was refluxed for ca. 3 hr. The whole was heated under diminished pressure to remove water produced and the unreacted acid. The porous solid material obtained was then dry-distilled and finally under a diminished pressure. The crude ketone was washed with a concentrated solution of potassium carbonate, dried over calcium chloride, and distilled. B. p. 122～128°;C the greater part distilled out at ca. 125°C. Yield, 35%.

The Formic Acid Rearrangement of III.—Twenty grams of III was refluxed with 160 g. of ca. 80% formic acid for ca. 80 min. and worked up as usual. The product was separated into three fractions: (1) b. p. 67～71°C (19 mm.), 11 g., yield 55%; (2) b. p. 72～80°C (19 mm.), 1g.; (3) b. p. 85～91C° (19 mm.), 1.2 g., yield 6%; residue, a small amount of red oil. All these fractions were colorless, hardly soluble in water, had a camphoraceous odor (fraction 3 was accompanied by a somewhat stimulative smell), and instantly decolorized bromine water. The forerun, b. p. ca. 50～67°C (19 mm.) (ca. 2.7 g.) was somewhat yellowish and seemed still to contain a small quantity of the unreacted carbinol, a few white precipitates being produced with ammoniacal silver nitrate.

9) A. F. Thompson, Jr. et al., *J. Am. Chem. Soc.*, **63**, 186 (1941).

Fraction 1 was believed to be *3-isopropyl-4-methyl-3-penten-2-one* (*III$_a$*)[5]; its nature coincided with that reported by Hickinbottom et al. They obtained the compound also from III with the aid of Rupe reaction.

Anal. Found: C, 75.87; H, 11.32. Calcd. for $C_9H_{16}O$: C, 77.09; H, 11.50%.

Somewhat greater deviation in the carbon content was due possibly to contamination with a compound enriched in oxygen, perhaps the acid formed on autoxidation of III$_b$.

This fraction, on treatment with 2,4-dinitrophenylhydrazine, only gave *an oily red derivative; the semicarbazone* could not be obtained. The fraction was refluxed with phenylhydrazine hydrochloride in ethanolic acetic acid, then water was added, and the brown oil separated out gave a pyrazoline reaction of deep bluish violet coloration with sodium nitrite and sulfuric acid.

The same fraction was hydrogenated with palladium to yield an oil of strongly camphoraceous odor, which afforded an oily yellow 2,4-dinitrophenylhydrazone.

Fraction 3 (*3-isopropyl-4-methyl-2-pentenal, III$_b$*) was positive toward Schiff test (violet color was gradually produced and turned deep pink-purple on standing), and reduced ammoniacal silver nitrate. That the greater part of this fraction consisted of the single compound was ascertained from the quantity obtained of its 2,4-dinitrophenylhydrazone.

The same fraction on being treated with phenylhydrazine in the manner indicated above, gave a brown oil which had a pyrazoline reaction of deep violet coloration.

2,4-Dinitrophenylhydrazone of III$_b$ was recrystallized from pyridine containing a little ethanol, light red plates, m. p. 173.5~174°C (reported m.p. 151.5~153°C)[6]. The derivative became thick deep red prisms or needles when allowed to stand overnight in the acidic reagent (the 2,4-dinitrophenylhydrazine reagent was applied as a methanolic sulfuric acid solution). The melting point of the thick crystals was identical with that of the light red plates, the mixed melting point was undepressed. The light red plates also were converted into the thick crystals on several hours' standing in methanol containing a little sulfuric acid.

Anal. Found: N, 17.52. Calcd. for $C_{15}H_{20}O_4N_4$: N, 17.49%.

Semicarbazone of III$_b$ was recrystallized from methanol, colorless micro-needles, m. p. 208~210°C.

Anal. Found: N, 21.56. Calcd. for $C_{10}H_{19}ON_3$: N, 21.30%.

Hydrogenation Product of III$_b$ (IV).—Half a gram of fraction 3 was hydrogenated in ether with palladium. The reaction product, freed from the ether, was positive toward Schiff test, deep pink color (tinged with purple) being gradually produced. IV was considered to be *3-isopropyl-4-methylpentanal* (*IV*).

2,4-Dinitrophenylhydrazone of IV was recrystallized from pyridine-methanol, yellow plates, m. p. 86~88°C.

Anal. Found: C, 55.67; H, 6.62; N, 17.67. Calcd. for $C_{15}H_{22}O_4N_4$: C, 55.88; H, 6.88; N, 17.38%.

Fraction 2.—The intermediate fraction contained a considerable quantity of III$_b$ as the 2,4-dinitrophenylhydrazone.

The initial distillate of the forerun in the case of fractionation of the rearrangement product, which was collected at ca. 51°C (19 mm.) and weighed 0.2 g., afforded a small amount of 2,4-dinitrophenylhydrazone of yellow plates, m. p. ca. 124°C (from pyridine-methanol). It seemed to be possibly the derivative of acetone produced by hydrolytic fission of III$_a$; the amount was insufficient for rigid identification.

Summary

The behavior of 3,4-dimethyl-1-pentyn-3-ol (II) and 3-isopropyl-4-methyl-1-pentyn-3-ol (III) toward formic acid was investigated. The carbinols, as in the previous report[1], were chosen as model ones in which the tertiary carbon atom is adjacent to the carbon atom carrying the hydroxyl group. Both carbinols gave a significant quantity of the respective aldehydes. These aldehydes were easily isolated on simple distillation.

II gave 3,4-dimethyl-3-penten-2-one (II$_a$) in 45% yield and 3,4-dimethyl-2-pentenal (II$_b$), a new aldehyde, in 5% yield. III gave 3-isopropyl-4-methyl-3-penten-2-one (III$_a$) in 55% yield and 3-isopropyl-4-methyl-2-pentenal (III$_b$) in 6% yield. These carbonyl compounds were characterized. III$_b$ was hydrogenated to give 3-isopropyl-4-methylpentanal (IV) as the 2,4-dinitrophenylhydrazone.

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Studies on the Antitubercular Compounds. XVI. Preparation of Some Derivatives of 2,1,3-Benzothiadiazole***

By Isao SEKIKAWA

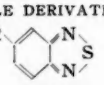
(Received November 19, 1958)

In a previous paper[1] the author has reported the syntheses of several kinds of 4- and 5-substituted 2,1,3-benzothiadiazole compound. These compounds have been shown to have no antitubercular activity in vitro. In the present paper, the new compounds listed in Table I and Table II were prepared in order to increase the antibacterial effect of the compounds of this series against *Mycobacterium tuberculosis*. 5-Bromomethyl-2,1,3-benzothiadiazole (I) was prepared by bromination of 5-methyl-2,1,3-benzothiadiazole with *N*-bromosuccinimide by the usual method, and readily converted into aminomethyl hydrochloride (II) by the Delepine reaction[2].

2,1,3-Benzothiadiazole-5-aldehyde (VI) was prepared from I in excellent yields through the hexaminium salt by Sommelet reaction[3]. Reaction of 2,1,3-benzothiadiazole with *N*-methylformanilide and phosphorous oxychloride in *o*-dichlorobenzene gave no formyl compound.

VI was readily oxidized into 5-benzothiadiazolecarboxylic acid (III) by the Delepine's method[4] in an alcoholic solution.

TABLE I. 5-SUBSTITUTED 2,1,3-BENZOTHIADIAZOLE DERIVATIVES



I	$-CH_2Br$
II	$-CH_2NH_2 \cdot HCl \cdot H_2O$
III	$-COOH$
IV	$-CONHNH_2$
V	$-CONH_2$
VI	$-CHO$

By the oxidation of 5-methyl-2,1,3-benzothiadiazole with potassium permanganate, not only methyl group but also benzene nucleus was attacked, so that III could not be obtained. Chlorination of III with thionyl chloride afforded an acid chloride, which was smoothly converted into acid amide V. Acidhydrazide IV was prepared from III by the usual method. Semicarbazone (VII), thiosemicarbazone (VIII), picolinoylhydrazone (IX), nicotinoylhydrazone (X) and isonicotinoylhydrazone (XI) were derived from VI by condensation with semicarbazide, thiosemicarbazide, α-, β- and γ-pyridinecarbohydrazide, respectively.

A detailed report on the antitubercular activity of these compounds will appear elsewhere.

Experimental

I.—A mixture of 4.5 g. of 5-methyl-2,1,3-benzothiadiazole, 5.4 g. of *N*-bromosuccinimide and 150 ml. of tetrachloromethane was refluxed for 18 hr. After cooling in ice bath, succinimide was removed by filtration and washed with 50 ml. of tetrachloromethane. After removing tetrachloromethane, the solidified residue was recrystallized from methanol to give 4.9 g. (70%) of lachrymatory white needles, m. p. 89~90°C.

Anal. Found: C, 36.41; H, 2.36. Calcd. for $C_7H_5N_2SBr$: C, 36.70; H, 2.20%.

II.—To a solution of 2.3 g. of I in 22 ml. of chloroform, 1.4 g. of hexamethylenetetramine was added. The mixture was allowed to stand overnight at room temperature, and the hexaminium salt was filtered and washed with 20 ml. of ether; yield 3.5 g., m.p. 182°C (decomp.)

A mixture of 1.2 g. of the hexaminium salt, 3 ml. of concentrated hydrochloric acid and 7 ml. of water was refluxed for 30 min., and the reaction mixture was concentrated to dryness under reduced pressure. The residue was recrystallized from water to give 0.4 g. of white needles, which softened at 235°C, became brown and decomposed at 245~246°C.

Anal. Found: C, 38.24; H, 4.87; H_2O, 8.10. Calcd. for $C_7H_5N_3S \cdot HCl \cdot H_2O$: C, 38.27; H, 4.59; H_2O, 8.20%.

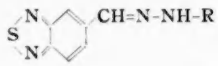
VI.—A mixture of 3 g. of the hexamethylenetetramine salt, 0.1 g. of hexamethylenetetramine and 6 ml. of 50% acetic acid was refluxed

* This paper constitutes a part of a series entitled "Studies on the Antitubercular Compounds", by S. Kakimoto. Paper XV, S. Kakimoto and J. Nishie, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **79**, 1403 (1958).

** A part of this study was presented at the Annual Meeting of the Chemical Society of Japan in Tokyo on April 3, 1958.

1) I. Sekikawa, This Bulletin, **31**, 252 (1958).
2) M. Delepine, *Compt. rend.*, **120**, 501 (1895).
3) M. Sommelet, ibid., **157**, 852 (1913).
4) M. Delepine and P. Bonnet, *Bull. soc. chim. France*, (4) **5**, 879 (1909).

TABLE II.



No.	R	m.p. (°C)	Appearance	Formula	Analysis (%) Calcd. C.	H.	H_2O	Found C.	H.	H_2O
VII	$-CO-NH_2$	251~252 d.*	White needles	$C_8H_7ON_3S$	43.43	3.19		43.09	3.37	
VIII	$-CS-NH_2$	228 d.	Yellow needles	$C_8H_7N_3S_2$	40.49	2.97		40.41	3.13	
IX	$-CO-C_5H_4N$ (α)	233~235	Pale yellow needles	$C_{13}H_9ON_3S$	55.11	3.20		55.13	3.51	
X	$-CO-C_5H_4N \cdot 2H_2O$ (β)	216~217	Pale yellow needles	$C_{13}H_{13}O_3N_3S$	48.89	4.10	11.28	48.86	4.43	11.16
XI	$-CO-C_5H_4N \cdot H_2O$ (γ)	218~219	White needles	$C_{13}H_{11}O_2N_3S$	51.82	3.68	5.98	51.63	3.91	6.09

* Decomp.

for 20 min. On cooling, a solid resulted. Recrystallization from methanol afforded 0.6 g. (47%) of white needles, m. p. 94°C.

Anal. Found: C, 51.25; H, 2.56. Calcd. for $C_7H_4ON_2S$: C, 51.21; H, 2.46%.

III.—To a solution of 0.9 g. of VI in 30 ml. of ethanol 2.3 g. of silver nitrate dissolved in 3 ml. of water was added. To the mixture was added 1.5 g. of sodium hydroxide in 10 ml. of water in small portions under stirring.

After being kept overnight, the deposited silver was removed and washed with 10 ml. of water. The solution was acidified with acetic acid to give an orange precipitate which was recrystallized from water to give 0.3 g. of white sandy crystals. It softened at 214°C and melted at 224~225°C.

Anal. Found: C, 46.63; H, 2.57. Calcd. for $C_7H_4O_2N_2S$: C, 46.66; H, 2.24%.

V.—A mixture of 0.4 g. of III and 5 ml. of thionyl chloride was refluxed for 1 hr. The excess of thionyl chloride was removed in a vacuum desiccator. The residue was dissolved in ether, saturated with ammonia and kept at room temperature for 1 hr. After removing ether, the solidified residue was recrystallized from water to give 0.3 g. of white needles, m.p. 202~203°C.

Anal. Found: C, 46.96; H, 3.01. Calcd. for $C_7H_5ON_3S$: C, 46.92; H, 2.81%.

IV.—A mixture of 0.15 g. of III, 3 ml. of absolute ethanol and 0.3 ml. of concentrated sulfuric acid was refluxed for 8 hr. After removing ethanol, the residue was treated with water and neutralized with sodium hydrogen carbonate. The resulting gray solid was heated with 0.1 ml. of hydrazine hydrate (80%) in 5 ml. of ethanol for 8 hr. The mixture was evaporated to dryness and the residue was recrystallized from water to give 0.1 g. of white needles, m.p. 180~181°C (decomp.).

Anal. Found: C, 42.99; H, 3.21. Calcd. for $C_7H_6ON_4S$: C, 43.29; H, 3.11%.

IX.—A mixture of 0.2 g. of VI, 0.16 g. of picolinic acidhydrazide and 5 ml. of ethanol was refluxed for 1 hr. The product was collected and recrystallized from ethanol to give 0.3 g. of yellow needles, m. p. 233~235°C.

Anal. Found: C, 55.13; H, 3.51. Calcd. for $C_{13}H_9ON_3S$: C, 55.11; H, 3.20%.

VII, VIII, X and **XI** were prepared by analogous methods.

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The Mechanical Behavior of Swollen Polystyrene, Poly-p-chlorostyrene and their Copolymers in Benzene. I. The Degree of Polymer-solvent Interaction and Thermoelastic Properties

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(Received November 26, 1958)

In the previous papers[1], the influence of the polymer-solvent interaction upon the mechanical properties of the swollen polymethyl acrylate gels was discussed, and it was shown that the mechanical properties of these gels having various degrees of swelling can be interpreted as the function of the interaction force between polymer chains. The intermolecular force between chain polymers was controlled, however, by giving the different degrees of swelling through the use of several organic solvents of different solvent power.

It is interesting to examine, in the next step, how the mechanical properties of gels in a swelling equilibrium with solvents are influenced by the structural units in a polymer molecule.

In this paper, polystyrene, poly-*p*-chlorostyrene and their copolymers, slightly cross-linked with divinyl benzene, are carried into the swelling equilibrium in benzene, and the mechanical properties of these gels are studied.

At the swelling equilibrium with excess solvent, the following equation holds[2]

$$\ln(1-v_r)+v_r+\mu v_r^2=-\rho V_0 v_r^{1/3}/M_c$$

where v_r is the volume fraction of polymer, ρ the density of pure solvent, V_0 the molar volume of solvent, M_c the average molecular weight of polymer between junction points and μ a parameter which indicates the type and degree of interaction exhibited by the polymer-liquid system.

In the region in which the stress-strain curve is reversible, the force f required to extend a specimen to an extension ratio λ is given by[3]

$$f=2Av_r^{-1/3}(\lambda-\lambda^{-2})(C_1+\lambda^{-1}C_2) \qquad (1)$$

where A is an unstrained area of cross section in the dry state, and C_1 and C_2 are the parameters relating to the mechanical properties of the specimen.

At a high degree of swelling, we can obtain the following relation from statistical consideration,

$$C_1=1/2RTM_c^{-1}$$

From these relations, the next equation follows,

$$-\ln(1-v_r)-v_r-\mu v_r^2=2V_0C_1v_r^{1/3}/RT \qquad (2)$$

Thus, we can estimate the value of C_1 from Eq. 1 by plotting the value of $f\{2A_0(\lambda-\lambda^{-2})\}^{-1}v_r^{1/3}$ against λ^{-1} in the results of the stress-strain measurements, and then can obtain the parameter μ from Eq. 2 using this value of C_1.

On the other hand, the following thermodynamic relations can be deduced.

$$(\partial G/\partial\lambda)_T=fl_0 \qquad (3)$$

$$T(\partial S/\partial\lambda)_T=-Tl_0(\partial f/\partial T)_\lambda \qquad (4)$$

$$(\partial H/\partial\lambda)_T=T(\partial S/\partial\lambda)_T+(\partial G/\partial\lambda)_T \qquad (5)$$

where G is the freee energy, H the enthalpy and S the entropy. From the above relations, we can estimate the change of the thermodynamic functions by measuring initial stresses at various strains and temperatures.

Experimental

Samples.—Commercial monomeric styrene and divinyl benzene were purified by fractional distillation under the reduced pressure after the removal of inhibitor with aqueous alkaline solution.

Benzene was purified by the ordinary method. *p*-Chlorostyrene was synthesized in the following way[4]. Purified commercial mono-chlorobenzene reacts with acetyl chloride in the presence of aluminum chloride (Friedel-Crafts' reaction), and the *p*-chloroacetophenone thus obtained was reduced to *p*-chloro-phenylmethylcarbinol by isopropyl alcohol saturated with aluminum isopropylate prepared freshly before

1) K. Ogino, This Bulletin, **31**, 577, 580, 584 (1958).
2) P. J. Flory and J. Rehner, *J. Chem. Phys.*, **11**, 512 (1943); M. L. Huggins, *J. Am. Chem. Soc.*, **64**, 1712 (1942).
3) R. S. Rivlin and D. W. Saunders, *Phil. Trans.*, **A243**, 251 (1951).
4) E. Matui, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **45**, 1094 (1942).

the reaction. Finally this carbinol was dehydrated by potassium bisulfate in the presence of picric acid[5] under reduced pressure.

Six cc. of styrene, or *p*-chlorostyrene or a mixture of these two monomers was polymerized with about 0.01 cc. of divinyl benzene in bulk in a sealed glass tube by the method described in the previous paper[1].

The polymer block was then cut into several parts about 1 cm. in length by a turning lathe. Care was taken so that the error in the diameter of the specimen was confined within 10^{-3} cm. These polymer rods were then dipped in the excessive amount of benzene, and brought into the swelling equilibrium.

Apparatus. — The apparatus used in this experiment is the same as that used in the previous experiment[1], and is shown in Fig. 1.

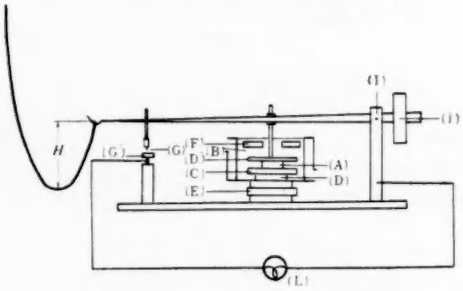

Fig. 1. The apparatus used in this experiment. (A), Specimen; (B), Solvent; (C), Iris; (D), Pressure plate; (E), Screw; (F), Desiccating agent; (G & G'), Contact; (J), Balancing weight.

The specimen in the swelling equilibrium with the solvent is placed between a flat brass block (D) and a pressure plate (D') in the solvent, and is strained vertically to a given extent, by rotating the screw (E) which is graduated to 1/100 mm. The initial stress is measured by the chain (H) using the value of its linear density.

The temperature of the specimen was controlled by circulation of water within the range of ± 0.5°C.

Results and Discussion

The plot of $f\{2A(\lambda-\lambda^{-2})\}^{-1}v_r^{1/3}$ against λ^{-1} at 25°C is shown in Fig. 2, and the values of μ for each polymer are given in Table I.

TABLE I. THE VALUE OF μ IN BENZENE AT 25°C

Polymer	μ
Polystyrene	0.47
Poly-*p*-chlorostyrene	0.49$_5$

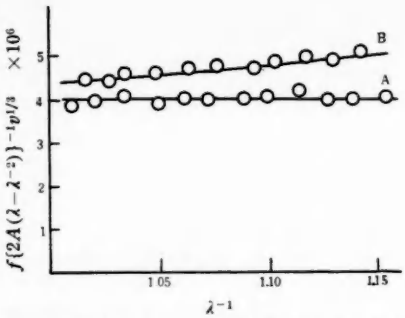

Fig. 2. Diagram of $f\{2A(\lambda-\lambda^{-2})\}^{-1}v_r^{1/3}$ against λ^{-1} for polystyrene-benzene (A) and poly-*p*-chlorostyrene-benzene (B) at 25°C.

The thermodynamic quantities in Eqs. 3, 4 and 5 at 25°C are shown in Figs. 3—6.

The value of μ of 0.47 for the system polystyrene-benzene differs from the value 0.453 by Boyer and Spencer[6] in their study of the stress-strain properties of this system.

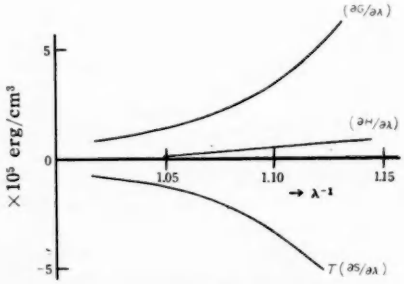

Fig. 3. Thermodynamic relation. Monomer ratio, Styrene 5 : *p*-Chlorostyrene 0

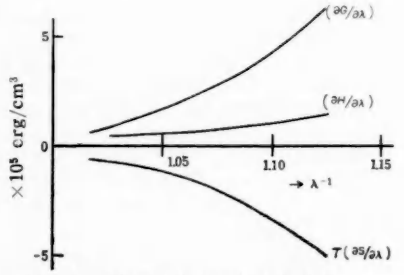

Fig. 4. Thermodynamic relation. Monomer ratio; Styrene 3 : *p*-Chlorostyrene 2

5) H. R. Snyder et al., "Org. Syntheses", Vol. 28, John Wiley & Sons, New York (1948), p. 31.

6) R. F. Boyer and R. S. Spencer, *J. Polymer Sci.*, **3**, 97 (1948).

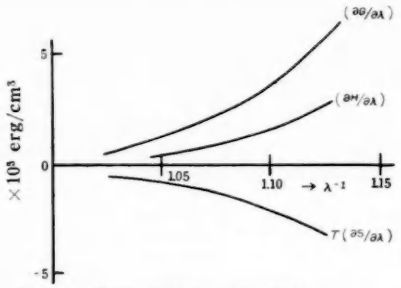

Fig. 5. Thermodynamic relation.
Monomer ratio; Styrene 2 : *p*-Chlorostyrene 3

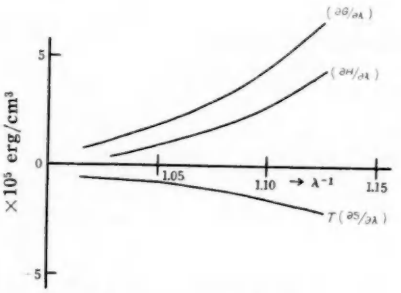

Fig. 6. Thermodynamic relation.
Monomer ratio; Styrene 0 : *p*-Chlorostyrene 5

Such a difference as this is also found among the other workers: Rivlin et al.[7] obtained the value of μ of 0.42 for natural rubber-benzene, and compared it with the value of 0.395 reported by Gee*. These two values were obtained from the stress-strain measurement of swollen rubbers. The measurements were conducted in ways similar to each other. Rivlin et al. considered that the source of the larger value of μ obtained in their investigation might be due to the degradation of the rubber during prolonged swelling in solvent in the determination of v_r.

An alternative source for the discrepancy in the values of μ originates from the effect of cross-linking as mentioned in the previous paper[1].

The fact that the value of μ of poly-*p*-chlorostyrene (0.49_5) is greater than that of polystyrene (0.47) shows that benzene is not so good a solvent for poly-*p*-chlorostyrene as for polystyrene. This may be due to the substituted chlorine atoms, for there appears a large polarity, and greater interaction may arise between long chain molecules. Thus, polymer-polymer contacts increase by the presence of chlorine atoms, and hence μ becomes larger.

The gradient of the curves of $f\{2A(\lambda-\lambda^{-2})\}^{-1}v_r^{1/3}$ against λ^{-1} is identical with C_2. It is well known that[3] the value of C_2 depends on the degree of swelling, v_r, and is found to be independent of the nature of the rubber polymer, the degree of vulcanization, and of the nature of the swelling liquid. It is associated primarily with the existence of secondary network. The experimental data in Fig. 2 shows a good linear relationship for these two polymers, and the gradients of these two lines, or C_2, are nearly equal to zero. But if we compare poly-*p*-chlorostyrene gel with polystyrene gel, the former has a slightly larger positive value of C_2. From this fact, it is reasonable to assume that the larger restriction to the possible configuration of the molecular chain exists in poly-*p*-chlorostyrene gel, and so the interaction force between long chain molecules can be considered to be stronger.

Deutsch, Hoff and Reddish[8] and also Scott and Magat[9] discussed the effect of some polar groups upon the mechanical and dielectric properties, or upon the cohesive energy density of polymer, and their results support the above consideration**.

The strength of intermolecular force between chain molecules is also estimated from the change of thermodynamic functions. The increase of chlorine content in copolymers corresponds to the large contribution of the term $(\partial H/\partial\lambda)$ to $(\partial G/\partial\lambda)$. The function H can be considered as the internal energy, and the large value of a change of this term may be due to the strong interaction between chlorine atoms, i. e., the change of internal energy when a strain increases is increased by the introduction of a stronger intermolecular force. As these systems are in the same solvent and have a nearly equal volume fraction v_r, we can assume that

7) S. M. Gumbrell, L. Mullin and R. S. Rivlin, *Trans Faraday Soc.*, **49**, 1495 (1953).

* Gee has also reported the other value of μ of 0.41 from the vapor pressure measurement. Cf., *Trans. Faraday Soc.*, **42**, 507 (1946).

8) K. Deutsch, E. A. W. Hoff and W. Reddish, *J Polymer Sci.*, **13**, 565 (1954).

9) R. L. Scott and M. Magat, ibid., **4**, 555 (1949).

** The structural effect upon the melting point or freezing point has been summarized by Uematu. Cf., *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **59**, 750 (1956).

the change of the value of μ or of thermodynamic functions comes from the presence of chlorine atoms.

In the present discussion, the author considered that the effect of chlorine atoms may prevail upon their volume effect in relation to the mechanical properties, and took into account only this effect. But, of course, there must exist some volume effect of this polar group, and this is neglected in the above discussion.

The effect of intermolecular forces upon the other mechanical properties by introducing chlorine atoms is now under study.

In concluding this paper, the author wishes to express his thanks to Professor H. Akamatsu and Assistant Professor T. Nakagawa for the advice and guidance given him during his study.

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New Preparation of Diphenylsilanediol

By Toshio TAKIGUCHI

(Received November 29, 1958)

In separate papers[1,2] the author has described new methods of preparation of diphenylsilanediol (hereafter called diol), in which it has chiefly been aimed at for successful preparation to minimize the polymeric effect of hydrogen chloride produced thereby. In the present communication the author wishes to present some effective methods together with procedural details to prepare diol directly from diphenyldichlorosilane (DPDS). The first is the preparation from the reaction of DPDS with sodium or potassium hydrogen carbonate, the key feature of this method being the hydrolysis of DPDS with water produced by decomposition of the carbonates. The reaction can be represented summarily by the following equation for sodium hydrogen carbonate:

$$(C_6H_5)_2SiCl_2 + 2NaHCO_3 \rightarrow (C_6H_5)_2Si(OH)_2 + 2NaCl + 2CO_2$$

The fairly stable character of this diol has also prompted the second method which is possibly the simplest among the related works[3] and involves the direct hydrolysis of DPDS with a theoretical amount of water dissolved in inert organic solvents followed by complete removal of hydrogen chloride by using some appropriate reagents, e.g., calcium carbonate, sodium carbonate anhydride, calcium hydroxide, aniline or pyridine.

Experimental

Fine powdered inorganic salts in reagent-grades were used after prolonged drying in a vacuum-desiccator. Aniline and pyridine were distilled under reduced pressure after drying over potassium hydroxide. Reagent-grade acetone, benzene, ethyl acetate and ether were used without further purification. Highest-purity DPDS was received from the Shin-etsu Chemical Industrial Company.

(A) From the Reaction with Sodium or Potassium Hydrogen Carbonate.—Each carbonate undergoes reaction entirely similar to that of DPDS; a typical procedure is shown below. 25 g. (0.3 mol.) of sodium hydrogen carbonate and 200 ml. of acetone-benzene were placed in a one liter flask which had been kept in a water bath maintained at 50°C. A 25 g. portion (0.1 mol.) of DPDS dissolved in 50 ml. of acetone was added portion-wise to the flask which was shaken gently during the addition. On adding the silane solution, carbon dioxide was evolved readily and sodium chloride precipitated as fine white crystalline powder. After the addition was complete, the mixture was refluxed gently for 20 min. and then filtered under suction after cooling. On evaporating the filtrate to dryness on a water bath, a white crystalline mass was obtained from

1) "Hydrolysis of Diphenyldichlorosilane in the Presence of Aniline", *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **62**, 601 (1959).
2) "New Simple Preparation of Diphenylsilanediol", *J. Org. Chem.*, in the press.
3) W. Dilthey and F. Eduardoff, *Ber.*, **37**, 1139 (1904); G. Martin, ibid., **45**, 403 (1912); F. S. Kipping, *J. Chem. Soc.*, **101**, 2108 (1912); C. A. Burkhard, *J. Am. Chem. Soc.*, **67**, 2173 (1945); J. F. Hyde and R. C. DeLong, ibid., **63**, 1194 (1941); S. Fukukawa, *Science & Industry, Japan* (*Kagaku to Kogyo*), **30**, 71 (1956).

which 20 g. (93%) of pure diol was obtained by recrystallization from ethyl acetate.

(B) Direct Hydrolysis Method.—In a one liter flask, were placed 400 ml. of acetone-benzene and 7 g. (0.4 mol.) of distilled water. After the addition of 51 g. (0.2 mol.) of DPDS to the flask, the mixture was shaken gently for a few minutes. Then, fine powdered calcium carbonate was added portion-wise to the flask which had been preheated at about 50°C, whereby the carbonate decomposed exothermally, evolving carbon dioxide. The addition was continued until the crystal violet indicator (1 drop of 1% ethanol solution) which had been added gradually should acquire a distinct purple color. After the reaction was over, the mixture was treated similarly to A, yielding 39 g. (90%) of white needles.

The use of sodium carbonate in place of calcium carbonate yielded 84% (mean) of diol, while the use of calcium hydroxide gave a considerable amount of uncrystallizable oily product caused by the presumable polymeryzing effect of the hydroxide.

Lastly, the use of aniline[1] or pyridine as hydrogen chloride acceptor gave entirely similar results, whereby the hydrochloride of each base precipitated as fine crystalline powder, the yield of diol being 88~92%.

Some Properties of Diol.—The diol thus obtained has been identified by its infrared absorption data[4] and the interplaner spacing data[1] (by diffractometer). [Found: Si, 12.7; OH/molecule, 1.97 (Karl Fischer titration)[5]; mol. wt., 195~204 (glacial acetic acid)]. The density (measured in aqueous calcium chloride solution of the matched density) was 1.16. The melting point[6] showed a variety of 132~133, 142~144, 147~148, 155 and 158~160°C in spite of all careful measurements. Melting was always accompanied by decomposition and successive fusion always lowered the melting point.

The author gratefully acknowledges the helpful discussions with Dr. F. Hirata in whose laboratory this work was performed.

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4) W. S. Tatlock and E. G. Rochow, *J. Org. Chem.*, **17**, 1555 (1952).
5) H. Cilman and L. S. Miller, *J. Am. Chem. Soc.*, **73**, 2367 (1951).
6) Measured by using a clean Pyrex capillary tube and at the rate of heating 3~5°C per min., the bath being preheated at about 110°C.

*Dye-sensitized Photopolymerization of Vinyl Compounds. Polymerization of Styrene by Cyanine Dyes. III**

By Ai WATANABE

(Received December 3, 1958)

As reported in the previous papers[1,2], the photopolymerization of styrene occurs when the mixture of styrene and butanol (15 : 1 in volume) involving various cyanine dyes is irradiated by the visible light. The dye, at the same time, is bleached and it was concluded that both these reactions are initiated by a direct interaction between the excited dye molecule and the styrene. Generally speaking, however, the initial processes for the two reactions are not identical, since, for example, the number of kinetic chains for one decomposed dye molecule is a function of temperature. The participation of halogen ion in the reaction is highly plausible because of a marked difference between the rates for pinacyanol-iodide and -chloride. In order to elucidate the photochemical processes in these reactions, it would be desirable to compare the kinetic features of bleaching and polymerization, but only studies on the latter will be reported in this paper. Activation energies for the chain initiation were determined for various dyes and the influence of halogen species was examined. In addition, the following two facts which had been tentatively described in the previous paper[2] were reconfirmed: 1) light promotes only the initiation process of polymerization; 2) the concentration of dye

* Presented before the Ninth Annual Meeting of the Chemical Society of Japan, held at Kyoto, April 1956 and the Tenth Meeting at Tokyo, April 1957.
1) A. Watanabe and M. Koizumi, *J. Inst. Polytech. Osaka City Univ.*, **5C**, 114 (1956); M. Koizumi and A. Watanabe, This Bulletin, **28**, 136 (1955).
2) A. Watanabe and M. Koizumi, *J. Inst. Polytech. Osaka City Univ.*, **5C**, 124 (1956); A. Watanabe and M. Koizumi, This Bulletin, **28**, 141 (1955).

does not affect the rate in the region of $6.3\times10^{-6}\sim19\times10^{-6}$ mol./l.

Experimental

Material.—Styrene and *n*-butanol were purified in the same way as in the previous paper[1]. Isocyanine iodide, pinacyanol iodide and kryptocyanine iodide were granted by the late Dr. T. Ogata of the Institute of Physical and Chemical Research, Tokyo. All the other dyes except the above three were kindly supplied by the Japanese Research Institute for Photosensitizing Dyes, Co., Ltd. in Okayama.

Apparatus and Experimental Procedure.—The apparatus employed and the experimental procedure are mostly identical with the previous ones[1], but the dilatometric technique was adopted to follow the course of polymerization. The type of dilatometer was almost the same as used by Nakatsuka[3] except that a drum-type reaction cell of about 5 cc. in capacity was made of quartz and connected to a tube of hard glass. The reaction cell was arranged so as to let the parallel light beam illuminate the whole plane surface of the drum. Matsuda color filters were used; V-O 2 for pinacyanol, kryptocyanine and isocyanine, and V-Y 1 for trimethinthiocyanine.

One volume of *n*-butanol solution of dye was mixed with 15 volumes of styrene and the mixture was extensively evacuated. The concentration of the dye is always 1.2×10^{-5} mol./l. unless otherwise cited.

The extent to which the polymerization proceeded was calculated from the volume contraction, as performed by Burnett[4] employing the data of density for monomer and polymer reported by Patnode and Scheiber[5]. The average degree of polymerization was determined as in the previous paper[1].

Experimental Results

The Characteristics of the Bleaching Reaction.—The absorption spectra of various dyes employed are shown in Figs. 1 and 2. To avoid the overlapping of curves, the plot of $\log I_0/I$ is suitably displaced for some dyes, the magnitude of displacement being given by X. It is evident from these figures that in the butanol solution the position of absorption maximum is not affected by the kind of halogen, but in the styrene-butanol solution the maximum is more or less displaced to the longer wavelengths, the magnitude of shift being slightly different according to the species of dye and halogen.

The butanol solution of each dye does not bleach practically at 60°C even after

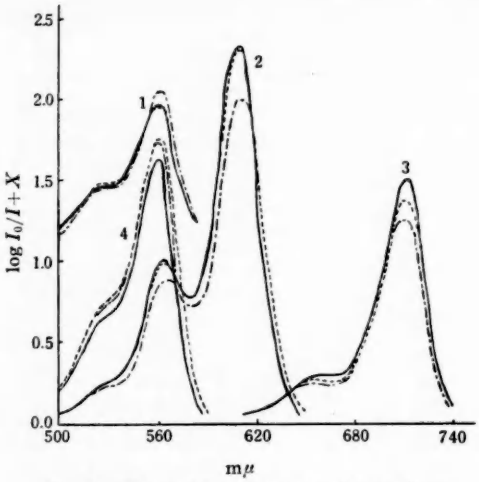

Fig. 1. Absorption spectra of cyanine dyes in *n*-butanol. Thickness of the cell, 1 cm.; 1.2×10^{-5} mol./l. (1, 2 and 4), 6.3×10^{-6} mol./l. (3). 1, isocyanine (X=1); 2, pinacyanol (X=0); 3, kryptocyanine (X=0); 4, trimethinthiocyanine (X=0). ——, iodide; ------, bromide; —·—, chloride.

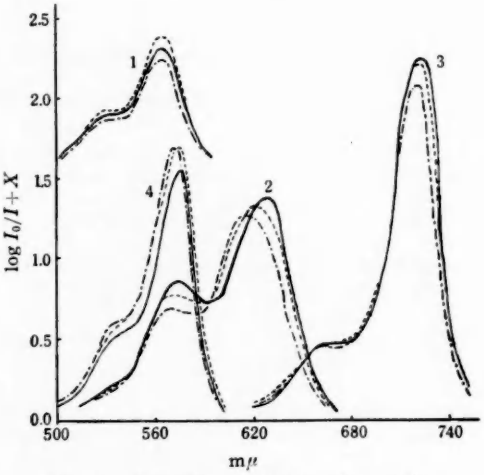

Fig. 2. Absorption spectra of cyanine dyes in styrene and *n*-butanol (15:1 in vol.). Thickness of the cell, 1 cm.; 1.2×10^{-5} mol./l. 1, isocyanine (X=1.5); 2, pinacyanol (X=0); 3, kryptocyanine (X=0); 4, trimethinthiocyanine (X=0). ——, iodide; ------, bromide; —·—, chloride.

illumination by the visible light for 6 hr. In the styrene-butanol solution, bleaching does not take place in the dark

3) K. Nakatsuka, S. Wada and M. Koizumi, *Chem. High Polymers* (*Kôbunshi Kagaku*), **14**, 609 (1957).
4) G. M. Burnett, *Trans. Faraday Soc.*, **46**, 772 (1950).
5) W. Patnode and W. J. Scheifer, *J. Am. Chem. Soc.*, **61**, 3449 (1939).

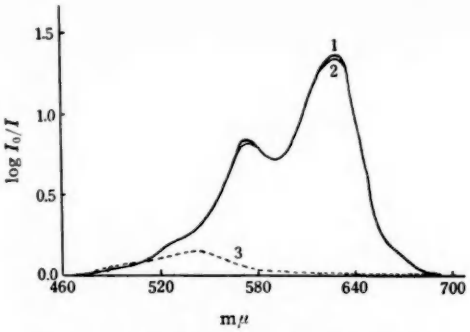

Fig. 3. Absorption spectra of pinacyanol iodide. 1, original sample; 2, after the reaction in dark for 2.5 hr. at 60°C; 3, after the reaction in light for 2.5 hr. at 60°C.

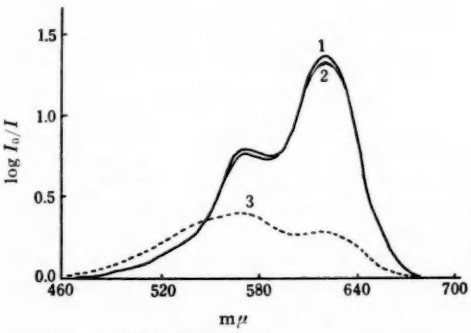

Fig. 4. Absorption spectra of pinacyanol bromide. 1, original sample, 2, after the reaction in dark for 5 hr. at 60°C; 3, after the reaction in light for 5 hr. at 60°C.

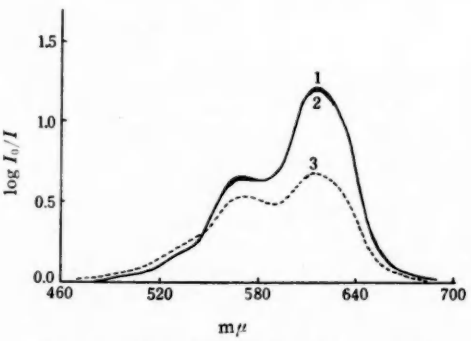

Fig. 5. Absorption spectra of pinacyanol chloride. 1, original sample; 2, after the reaction in dark for 5 hr. at 60°C; 3, after the reaction in light for 5 hr. at 60°C.

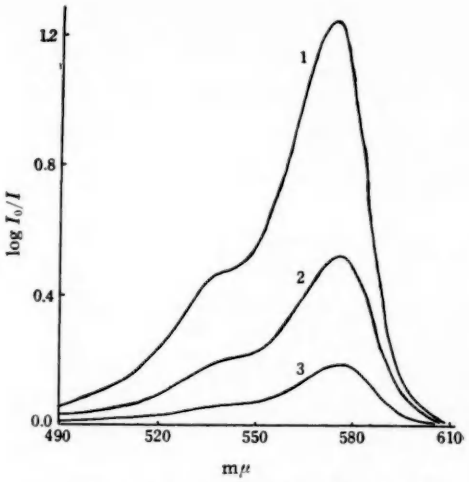

Fig. 6. Absorption spectra of illuminated trimethinthiocyanine. 1, chloride (60°C, 5 hr.); 2, bromide (60°C, 5 hr.); 3, iodide (60°C, 1 hr.).

(or does very slightly perhaps because of the dissolved oxygen or some impurities), but when illuminated, the bleaching occurs and at the same time the polymerization is promoted. The only curious exception is kryptocyanine bromide which is photobleached without inducing the polymerization, but retarding it very slightly at 60°C. Some of the absorption curves after the reaction for several hours are shown in Figs. 3, 4, 5 and 6. In case of pinacyanol, a new small absorption band appears in the visible region. So does it with isocyanine. In case of trimethinthiocyanine or kryptocyanine, the absorption curves merely decline over the whole visible region.

Effect of the Concentration of Dye.— Though it is a natural expectation that the rate of photochemical initiation is proportional to the intensity of light absorbed, there is some doubt about it under the present experimetal condition, since the dye of about 10^{-5} mol./l. in concentration absorbs nearly all the light and the distribution of the excited molecule in the system is not uniform. Hence it is desirable to check whether such a state of affairs does influence the rate or not. In the previous report it was perceived that the rate of polymerization is independent of the concentration of pinacyanol iodide in the range of $6\sim20\times10^{-6}$ mol./l. at 60°C, but this was not necessarily

conclusive since the styrene then used was not so carefully purified. Therefore the analogous experiment was repeated with more caution at 40°C. The results are tabulated in Table I. It is quite certain from Table I that the rate is completely independent of the dye concentration. In view of the absorbance of the dye the effective light is almost completely absorbed and the rate is not influenced by

TABLE I. EFFECT OF PINACYANOL IODIDE CONCENTRATION AT 40°C

Expt. no.	Dye concn. (10^{-6} mol./l.)	Relative rate (mm./hr.)
1	6.3	1.60
2	6.3	1.70
3	6.3	1.50
4	12	1.65
5	12	1.70
6	12	1.65
7	19	1.55
8	19	1.60

the dye concentration under the light intensity employed, but is determined by the quantity of excited dye produced in the whole system in a unit time.

The Relation between the Average Degree of Polymerization and the Overall Rate.—In the previous report[2], a test was made to see whether the irradiation only induces the chain initiation or also affects other steps such as propagation or termination. Using many data for several cyanine dyestuffs under various experimental conditions, the reciprocal of $\bar{P}_L$ (the average degree of polymerization for the polymer produced in the irradiated region of the reaction cell) was plotted against the overall rate V (the quantity of polymer produced in the irradiated region in a unit time). An approximately linear relationship was obtained supporting the view that the light only promotes the initiation process. But the points of data were not so satisfactory showing some scattering and it seemed desirable to repeat it again. In the present experiments, the solution of pinacyanol iodide of 1.2×10^{-5} mol./l. in concentration was used at 60°C and the intensity of light was varied by means of gauze wires. The results obtained by a similar treatment as in the previous paper are shown in Fig. 7. In this figure $\bar{P}_D$ is the average degree of polymerization in the dark part. The data are still distributed with some randomness, but in view of the fact that the value of $\bar{P}_D$ employed for the evaluation of

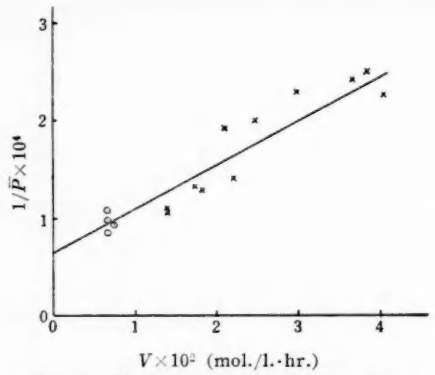

Fig. 7. Variation of the average degree of polymerization with the overall rate. ⊙, in dark; ×, in light.

$\bar{P}_L$ was a mean of many data in the dark, and further taking into account the poor reproducibility of the experiment the linearity can be regarded to hold.

Activation Energy.—The energy of activation was determined from rate measurements between 20° and 60°C under illumination and between 40° and 60°C in the dark using the dye solution of 1.2×10^{-5} mol./l. in concentration. The rate of photochemical reaction V_p was determined from the expression $V_p=\sqrt{V_l^2-V_d^2}$, where V_d is the rate of thermal reaction in the illuminated space and V_l is the total rate under illumination. The relation between $\log V_p$ and $1/T$ for various dyes is shown in Figs. 8, 9 and 10, where V_p are represented in per cent per hour. In case of pinacyanol iodide, V_p shows an abnormally high value at 50° and 60°C, but these are excluded from the calculation of

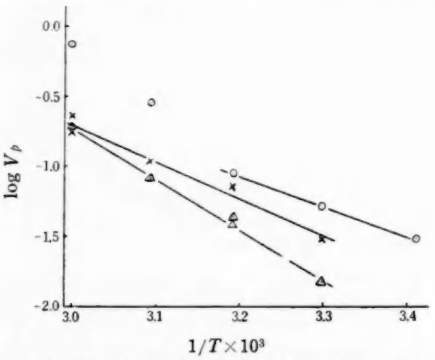

Fig. 8. Arrhenius plot for photopolymerization. ⊙, pinacyanol iodide; ×, pinacyanol bromide; △, pinacyanol chloride.

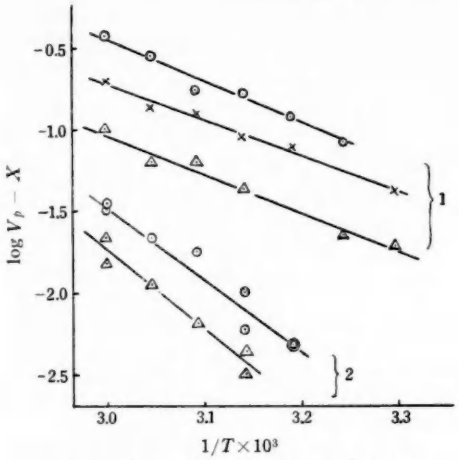

Fig. 9. Arrhenius plot for photopolymerization. 1, isocyanine (⊙, iodide (X=0); ×, bromide (X=0); △, chloride (X=0.4)); 2, kryptocyanine (⊙, iodide (X=1); △, chloride (X=1)).

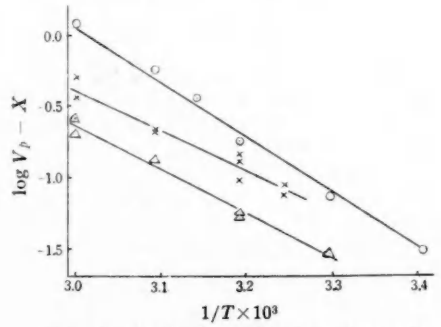

Fig. 10. Arrhenius plot for photopolymerization. Trimethinthiocyanine; ⊙, iodide (X=0); ×, bromide (X=0); △, chloride (X=0.3).

activation energy for the following reason. In the course of decomposition, this dye is transformed into a stable intermediate with a new visible absorption band, which is further decomposed by light absorption at 60°C accompanied with the induced polymerization. The above mentioned decomposition of the intermediate is far more rapid for iodide than for bromide or chloride as is evident from the Figs. 3, 4 and 5. Hence the polymerization induced by the decomposition of the intermediate is remarkable only for pinacyanol iodide at higher temperatures, while for bromide and chloride, in which similar intermediates are also produced, this secondarily induced polymerization is negligible at least in the initial stage of reaction due to their much lower rates of decomposition**. In case of isocyanine a new small peak also appears in the shorter wavelength region but the filter V-O 2 in this case does not transmit the light corresponding to the absorption of the intermediate, hence the polymerization due to its destruction will not take place. In case of kryptocyanine or trimethinthiocyanine the absorption declines monotonously in the whole visible region and the above considerations need not be taken into account. The values of the activation energy for the overall reaction thus evaluated are tabulated in Table II. By making use of Bamford's values[6] of activation energies for chain growth and chain termination (E_p=6.5 kcal./mol., E_t=2.8 kcal./mol.), the activation energy for initiation E_i can be calculated from the relation $E_i = 2E - 2E_p + E_t$. They are also included in Table II. Although the errors of these values are rather large owing to the poor reproducibility of experiments, some features can be seen and semi-quantitative discussions will be given below on the basis of these data.

TABLE II. ACTIVATION ENERGY
(kcal./mol.)

Dye	Dark-reaction		Photo-reaction	
	E	E_i	E	E_i
No dye	22.9	35.6		
Pinacyanol iodide	—	—	10.4	10.6
Pinacyanol bromide	21.6	33.0	12.1	14.0
Pinacyanol chloride	22.6	35.0	16.9	23.6
Kryptocyanine iodide	22.6	35.0	20.6	31.0
Kryptocyanine chloride	22.0	33.8	22.4	34.6
Isocyanine iodide	18.3	26.4	11.7	13.2
Isocyanine bromide	—	—	10.5	10.8
Isocyanine chloride	15.8	21.4	11.0	11.8
Trimethinthiocyanine iodide	—	—	17.4	24.6
Trimethinthiocyanine bromide	—	—	12.8	15.4
Trimethinthiocyanine chloride	22.0	33.8	14.2	18.2

Discussion

If the irradiation only promotes the

** Filter V-O 2 transmits the light including the absorption maximum of the intermediate as well as the two absorption peaks of the original dye.

6) C. H. Bamford and M. J. S. Dewar, *Proc. Roy. Soc.*, **A192**, 309 (1948).

chain initiation, then the following linearity between the reciprocal of $\bar{P}_L$ and V must hold as derived in a previous paper[2].

$$1/\bar{P}_L = k_t V/2k_p^2[M]^2 + (R_{tr\cdot M}[M] + k_{tr\cdot S}[S])/k_p[M] \quad (1)$$

where k_p, $k_{tr\cdot M}$, $k_{tr\cdot S}$ and k_t are the rate constants for propagation, monomer transfer, solvent transfer and termination, respectively, and $[M]$ and $[S]$ denote the concentrations of the monomer and the solvent, respectively. Under the present experimental conditions $k_{tr\cdot S}[S]$ can be neglected against $k_{tr\cdot M}[M]$, hence from the intercept and the inclination of the straight line in Fig. 7, $k_{tr\cdot M}/k_p$ and k_t/k_p^2 can be evaluated, to be 6×10^{-5} and 2.1×10^3 mol. l^{-1} sec., respectively. The value of $k_{tr\cdot M}/k_p$ obtained above shows an excellent coincidence with that reported by Mayo et al.[7] As for the value of k_t/k_p^2, Bamford's data[6], $k_t=4.6\times10^6$ l. mol^{-1} sec^{-1} and $k_p=60$ l. mol^{-1} sec^{-1} at 60°C, give $k_t/k_p^2=1.28\times10^3$ mol. l^{-1} sec., while Matheson's values[8], $k_t=7.2\times10^7$ l. mol^{-1} sec^{-1} and $k_p=176$ l. mol^{-1} sec^{-1}, give $k_t/k_p^2=2.32\times10^3$ mol. l^{-1} sec. and the present value is about the same as the Matheson's one. From the agreement of these constants it is certain that the irradiation only induces the chain initiation process and does not affect either the propagation nor the termination process. Thus there is no doubt that the mechanism of the photochemical initial process may be discussed on the basis of the values of E_i tabulated in Table II.

Table II indicates that mere interchange of the halogen often results in a marked change in E_i-value and it can be concluded that the halogen ion plays an essential rôle in the primary photoprocess. Next, broadly speaking, a tendency is noted that the larger the frequency of absorbed light, the smaller is the value of E_i. In the following, some considerations will be given about these results more closely.

From the fact that bleaching does not occur in the absence of monomer, there is no doubt that the photochemical process takes place between the excited dye and the monomer. Further the chain initiation of polymerization is considered to be induced by a radical, since the quantitative aspects of polymerization such as the values of k_t/k_p^2 and $k_{tr\cdot M}/k_p$ coincide with the data for the well-established radical polymerization. Of course, a detailed description of the photochemical primary process is beyond the scope of the present stage of investigation, but some consideration about it will be helpful for further investigation.

As regards the formation of the radical, it seems natural to suppose that in the course of attack of a styrene molecule on dye, an electron-transfer occurs, the electron of a halogen anion being transferred to a dye cation. Then, the styrene molecule may seize a halogen atom and the two radicals produced may sometimes both induce the chain-initiation, or otherwise the dye-radical produced may decompose of itself.

It will be described in the following how the above idea is materialized and how it can explain the present results. Firstly, according to the above idea, the photochemical primary process may be pictured as follows:

$$\underset{\text{Initial state}}{D^{+}{}^{*}\cdots X^{-}} + M \rightarrow \underset{\text{Activated state}}{D\cdots X\cdots M} \rightarrow \underset{\text{Final state}}{D\cdot} + MX\cdot$$

where D^+ and X^- are a dye cation and a halogen anion, respectively. The activated state would have a configuration in which an electron is transferred from X^- to D^+ and a bond is partially formed between X and M, these two processes chiefly determining the energy of the activated state.

In case of a common D, a) the ease of electron transfer would be in the order, I > Br > Cl, while b) the energy decrease due to X−M partial bond formation would be in the reversed order Cl > Br > I. If a styrene molecule is separated from D···X in the activated state, then a) would be a chief factor in determining the activation energy. On the contrary, when a styrene molecule is in close proximity to X, the activation energy would depend largely on b). Such would be the reason why the influence of halogen on activation energy is different in each dye.

In case of different D, the maximum of absorption differs and at the same time the tendency of electron transfer would also do so. Roughly speaking, these two factors would commonly act in the same direction for the following reason. The longer the wavelength of the absorption maximum which in many cases is caused by the longer chain of conjugation, the higher the highest occupied level

7) F. R. Mayo, R. A. Gregg and M. S. Matheson, *J. Am. Chem. Soc.*, **73**, 1691 (1951).
8) M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, ibid., **73**, 1700 (1951).

(or the lowest vacant level) lies and an electron is expected to transfer from X^- to D^+ with more difficulty. Thus it is expected that activation energy becomes greater as the absorption band is situated in the longer wavelength. This expectation is in accord with a general trend of the results.

The above qualitative discussion can be stated in much clearer form for an ideal case in which only the electron transfer

$$(D^+X^-)^* \rightarrow D \cdot X \cdot$$

is essential. It would be convenient to discuss this problem in terms of potential energy curves drawn against the distance between D and X. In Fig. 11, 1 is a

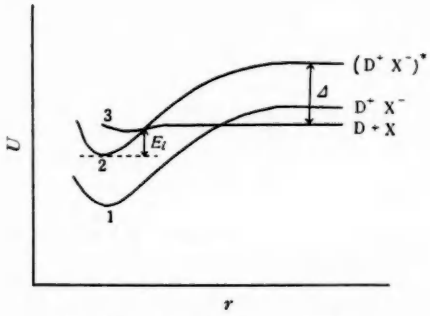

Fig. 11. Potential energy diagram.

potential energy curve of a dye in the ground state which is chiefly determined by the coulombic attraction between the solvated ions. 2 is the one of the excited dye, and 3 is a curve for the system after the electron is transferred from a halogen anion to a dye cation. The relative positions of the three curves are arbitrarily chosen but this does not essentially affect the discussion. Now at a larger distance, the energy difference between 2 and 3, Δ, is given by the equation

$$\Delta = I_D - A_X + h\nu - S \qquad (2)$$

where I_D is the ionization potential of a dye radical, A_X, the electron affinity of a halogen atom, $h\nu$, the energy of an absorbed quantum and S, a correction term related with the energy of solvation.

If the potential minimum in 1 and 2 is given by $e^2/\varepsilon r_X$ where r_X is the D−X distance in the minimum and ε is the effective dielectric constant, then the energy of activation is given by the following equation,

$$E_i = e^2/\varepsilon r_X - \Delta$$
$$= e^2/\varepsilon r_X - I_D + A_X - h\nu + S \qquad (3)$$

For a series of cyanine dyes with various halogens, E_i is determined by the value of

$$(e^2/\varepsilon r_X + A_X + S_X) = \delta_X$$

A_X for iodine, bromine and chlorine is respectively $72 < 81 < 87$ kcal./mol.[9] and S_X is most certainly in the same order. $e^2/\varepsilon r_X$ cannot always be determined by the size of a free ion, but may depend rather on the degree of solvation. In the former case it is in the order Cl > Br > I while in the latter case it might be reversed. If the magnitude of δ_X is mainly determined by $A_X + S_X$ then the activation energy will be in the order Cl > Br > I. Such would be the case for pinacyanol. The fact that there is no great difference in the values of E_i for isocyanine and kryptocyanine might be due to the participation of X−M bond energy in the activated state or to the contribution of $e^2/\varepsilon r_X$ in the inverse order depending on the structure of dye. In this connection, it seems suggestive that for trimethinthiocyanine and pinacyanol for which halogen anion can be placed naturally in between two N atoms, the value of E_i is much dependent on X, while for isocyanine and kryptocyanine for which halogen ion has to be situated in the neighborhood of one N atom apart from the other, the value of E_i is scarecely dependent at all on X. But it is a problem for the future why in the former pair, trimethinthiocyanine and pinacyanol, the effect of halogen is roughly in the inverse order.

Eq. 3 can also give a plausible interpretation of the results for various dyes with common X. With larger ν, I_D perhaps will also become larger, especially in cases when ν is largely dependent on the length of the chain and this causes E_i to become smaller. This is a general tendeny already mentioned.

Although a conclusive statement must await further investigation, the general feature of scheme would be as pictured above.

Summary

Extensive studies on the photopolymerization of styrene by virtue of cyanine dyes were performed and it was reconfirmed

9) A. Eucken and Landolt-Börnstein, "Zahlenwerte und Funktionen", I. Band, 1. Teil. Springer-Verlag, Berlin (1950), p. 213.

that only the chain initiation is promoted by the direct interaction between the excited dye and the styrene molecule. Activation energies for the photochemical initiation process were experimentally determined for several dyes of iodide, bromide and chloride. In general the activation energy depends on the kind of halogen ion and from this result it was concluded that halogen ion plays an essential rôle in the reaction. A general tendency was observed that the activation energy diminishes as the wavelength of absorption maximum of dyes becomes shorter. A plausible scheme for the chain initiation process was given, in which an electron transfer from X^- to D^+ is involved in the process of activation.

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Oxidative Cleavage of 1-Phenyl-dialin with Peracetic Acid

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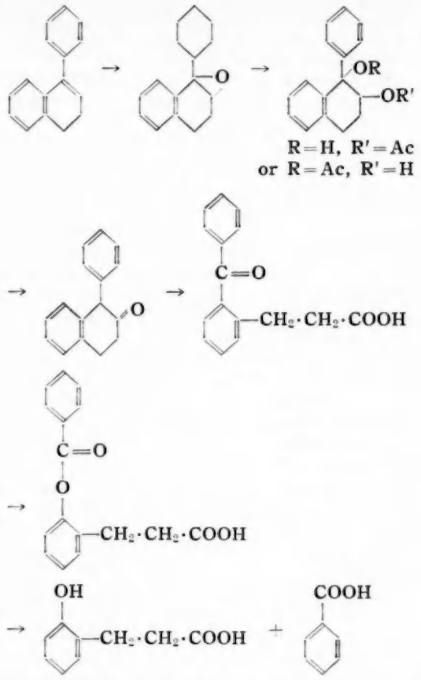
The present authors, recently, have carried out an extensive study on the oxidative cleavage of various compounds with peracetic acid, and it has been found that the hydroaromatic ring was readily dehydrogenated by peracetic acid. Our previous reports[1] indicated that the oxidative cleavage of dialin proceeded in two different reactions in an initial stage; the one was epoxidation and the other, dehydrogenation. On the contrary, the oxidative cleavage of 1-alkyl-dialin (4-alkyl-Δ^1-dialin) was shown to proceed by a predominant epoxidation with no dehydrogenation owing to the influences of alkyl groups.

In order to investigate the substituent-effects of phenyl group, the oxidative cleavage of 1-phenyl-dialin (4-phenyl-Δ^1-dialin) was carried out with peracetic acid. A mixture of 1-phenyl-dialin, ammonium molybdate and glacial acetic acid was heated at 40°C, and then 30% hydrogen peroxide solution was added. After the addition was completed, the reaction mixture was still maintained at the same temperature for further 12 hr.

From the neutral part, melilotine and 1-phenyl-tetralone-2 were isolated, and the presence of monoacetate of 1,2-dihydroxy-1-phenyl-tetralin was confirmed, but unreacted 1-phenyl-dialine was not found. Moreover, the products obtained from the acidic part were benzoic acid, melilotic acid and the benzoate of melilotic acid. The benzoate of melilotic acid was confirmed by elementary analysis, infrared spectrum measurement and hydrolysis. In the ultraviolet spectrum of the compound in 95% ethanol, the maximum absorption is present in 263 mμ ($\log \varepsilon$ 3.45) and 272 mμ ($\log \varepsilon$ 3.35). It is very interesting to note that no product formed by dehydrogenation was isolated.

From these results and also by analogy with the case of 1-alkyl-dialin, it was concluded that the reaction of peracetic acid with 1-phenyl-dialin proceeded by a predominant epoxidation with no dehydrogenation, followed by the oxidative cleavage. Although *o*-carboxyethyl-benzophenone could not be isolated, it might be considered to be the precursor of the benzoate of melilotic acid. Thus the essential steps in the reaction were as follows;

1) Y. Odaira and S. Tsutsumi, *Technol. Repts. Osaka Univ.*, 8, 455 (1958).



In order to obtain further evidence for the above sequence, an authentic 1-phenyl-tetralone-2 was oxidized with peracetic acid and the benzoate of melilotic acid, benzoic acid and melilotic acid were isolated in good yields as the oxidation products.

Compared with the case of 1-alkyl-dialin, it is very interesting that the Baeyer-Villiger reaction occurred because of the effect of phenyl substituent in this case.

It is generally accepted that, in the cleavage of unsymmetrical diaryl ketones[2] by the Baeyer-Villiger oxidation, the migrating group is normally the more electron-releasing one. For example, treatment of *p*-methyl-benzophenone with peracetic acid gives benzoic acid and *p*-cresol; that is, *p*-tolyl group migrates more readily than phenyl group. On the other hand, the oxidation of *o*-methyl-benzophenone with peracetic acid[3] leads to the mixture of *o*-tolylbenzoate (12%) and phenyl-*o*-toluate (38%). Therefore, it is obvious that the ortho-effect can even overcome, to some extent, an electronic effect in the opposite direction (*o*-tolyl vs. phenyl).

In the series $Ph\cdot(CH_2)_n\cdot COOH$ it was found that, whereas the absorption band of benzoic acid is at 268 mμ (ε 1780), the ω-phenyl fatty acids from phenyl-butyric acid upwards have the absorption maximum at 260 mμ with greatly reduced intensity (ε ca. 200), and that this absorption is almost identical in every respect with that of a mixture of ethylbenzene and acetic acid[4]. Moreover, *o*-toluic acid and *o*-carboxyethyl-benzoic acid have the same maximum band at 278 mμ ($\log \varepsilon$ 3.15 and 3.08, respectively).

From the above ultraviolet spectra results, it may be assumed that no resonance between carboxyl group and benzoyl group in the molecule of *o*-carboxyethyl-benzophenone exhibits, and the compound will be considered as identical with *o*-methyl-benzophenone from the electronic point of view. If the above concept is true, phenyl group should migrate more easily than *o*-carboxyethyl-phenyl group owing to the ortho-effect, and one would expect the stronger retarding effect of *o*-carboxyethyl group, since this group is bulkier than methyl group. Actually, the reverse result was obtained in our experiments; namely, only the benzoate of melilotic acid was isolated and the migration of *o*-carboxyethyl-phenyl group occurred predominantly.

A more plausible explanation of such an abnormal phenomenon appears to be the steric assistance caused by steric interference of *o*-carboxyethyl group. Further discussion of the problem of the steric assistance in the Baeyer-Villiger reaction now requires more detailed experiments.

Experimental

Reagent.—1-Phenyl dialin, (b. p. 178~180°C/12 mmHg; $n_D^{20.5}$ 1.6323), was prepared from tetralone-1 according to the procedure of Weiss[5] in 55% yield. Ultraviolet absorption spectrum: λ_{max} 227.5 mμ, $\log \varepsilon$ 4.26; 265.0 mμ, $\log \varepsilon$ 3.92; λ_{min} 248.0 mμ, $\log \varepsilon$ 3.84 (*iso*-octane). Infrared absorption spectrum: ν_{max} 1500, 1600 cm^{-1} (aromatics), 827 cm^{-1} ($CR_1R_2{=}CHR_3$); no OH band.

Oxidative Cleavage of 1-Phenyl-dialin.—A mixture of 1-phenyl-dialin (15 g.), ammonium molybdate (0.13 g.) and glacial acetic acid (240 cc.) was heated at 40°C, and then 30% hydrogen peroxide solution (30 cc.) was slowly added with stirring in the course of 2 hr. After the addition, the solution was maintained at the same temperature with continued stirring for another 12 hr. To the above solution was added hot water (350 cc.) with stirring to decompose most of unreacted peracetic acid and allowed to stand

2) C. Hassall, *Org. Reactions*, **9**, 73 (1957).
3) W. Saunders, *J. Am. Chem. Soc.*, **77**, 4679 (1555).
4) P. Ramart-Lucas, *Bull. soc. chim.*, **10**, 13 (1943).
5) R. Weiss, *Org. Syntheses*, **24**, 84 (1944).

for 2 days. The reaction mixture was concentrated as completely as possible on a steam bath under reduced pressure (40°C/20 mmHg).

The orange residue obtained was dissolved in ethyl ether (350 cc.), the ethereal layer was extracted with three 200 cc. portions of 10% aqueous sodium bicarbonate and divided into the ethereal layer (I) and the sodium bicarbonate solution (II). The ethereal layer (I) was washed with water and dried over anhydrous sodium sulfate. After evaporation, 5.5 g. of the yellowish residual oil was distilled under reduced pressure. The product, on fractionation, gave: (i) b. p. 120~140°C/6 mmHg (0.5 g., n_D^{28} 1.5560); (ii) b. p. 180~195°C/6 mmHg (2.7 g., n_D^{28} 1.6080); and (iii) dark orange residue (2.0 g.).

The fraction i, having the perfume like coumarine, showed the presence of lactone group (ν_{max} 1786, 1754 cm^{-1}) and ortho-substitution (ν_{max} 757, 746 cm^{-1}) in the infrared spectrum, and gave 0.32 g. of melilotic acid, m. p. 82~83°C, by hydrolysis with 25% potassium carbonate.

Melilotic acid obtained showed no melting point depression by mixing with the authentic melilotic acid prepared from coumarine. From these facts, the above fraction i was determined as melilotine.

The fraction ii gave a positive Brady's test and showed the presence of carbonyl group in the infrared spectrum. Oxime of the fraction ii was obtained as colorless needles, m. p. 184~185°C.

Anal. Found: N, 5.97. Calcd. for $C_{16}H_{15}ON$: N, 5.90%.

Lit. b. p. 156~158°C/1 mmHg (n_D^{24} 1.6089) for 1-phenyltetralone-2; m. p. 184~185°C for oxime of 1-phenyltetralone-2.

From these facts, the carbonyl compound obtained in the fraction ii was confirmed to be 1-phenyl-tetralone-2. A mixture of the fraction iii and 30% sulfuric acid (15 cc.) was heated under reflux for 3.5 hr. After cooling, the reaction mixture was treated in the usual ways and gave 0.8 g. of brown oil. The oxime obtained from the above oil melted at 184~185°C and weighed 0.34 g. Since the oxime was identified as the oxime of 1-phenyl-tetralone-2, it might be considered that monoacetate of 1,2-dihydroxy-1-phenyl-tetralin was contained in the fraction iii, the yield calculated from the oxime obtained was 0.402 g.

The above sodium bicarbonate solution II was acidified with dilute hydrochloric acid and saturated with sodium chloride and extracted with ethyl ether. The ethereal extract was washed with water and dried over anhydrous sodium sulfate. After the solvent was evaporated, 10.7 g. of crude acid was isolated. The crude acid was distilled under reduced pressure. The product, on fractionation, gave: i b. p. 125~200°C/7 mmHg (3.2 g.); and ii brown viscous residue.

The fraction i was recrystallized from water to 1.1 g. of colorless needles, m. p. 121°C. *p*-Bromo-phenacyl-ester of this crystal was obtained as colorless needles, m.p. 119°C. Since this crystal showed no melting point depression by mixing with pure benzoic acid, and the infrared spectrum of this crystal was in good agreement with that of pure benzoic acid, the above crystal was confirmed to be benzoic acid.

The above recrystallization mother liquor was extracted with ethyl ether and dried over anhydrous sodium sulfate. After the solvent was evaporated, the yellowish residual oil was distilled, giving a colorless oil, b. p. 265~275°C. Hydrolysis of this oil with 25% potassium carbonate gave 0.45 g. of colorless needles, m. p. 82~83°C, identified as melilotic acid by mixed fusion.

The fraction ii, a brown viscous residue, was dissolved in benzene-light petroleum ether (1 : 1) and chromatographed by passing the solution through a silica-gel column. The column was then eluted with benzene and evaporation of benzene from the effluent left 3.3 g. of colorless crystals, m. p. 144~145°C. Recrystallization from benzene afforded colorless needles, m. p. 145.5°C.

Anal. Found: C, 70.96; H, 5.47. Calcd. for $C_{16}H_{14}O_3$: C, 71.10; H, 5.22%.

Infrared analysis showed the absence of diarylketone group and hydroxyl group, whereas the presence of the hydroxyl stretching vibration of carboxyl group (ν_{max} 2700 cm^{-1}) and carbonyl group (ν_{max} 1730, 1706 cm^{-1}). *p*-Bromo-phenacyl-ester of the above crystals was obtained as colorless needles, m. p. 166~167°C.

In the ultraviolet spectrum of the above crystals, m. p. 145.5°C, the maximum absorption lies at 263 mμ ($\log \varepsilon$ 3.447) and 272 mμ ($\log \varepsilon$ 3.555) in 95% ethanol.

Moreover, hydrolysis of 2 g. of the above substance by sodium-alcoholat gave 0.78 g. of benzoic acid and 0.86 g. of melilotic acid. From these facts, the above substance was identified to be the benzoate of melilotic acid.

Oxidative Cleavage of 1-Phenyl-tetralone-2.—A mixture of 1-phenyl-tetralone-2 (2.5 g.), ammonium molybdate (0.02 g.) and glacial acetic acid (40 cc.) was heated at 40°C, and then 30% hydrogen peroxide solution (50 cc.) was slowly added with stirring. After the addition, the reaction mixture was kept at the same temperature with continued stirring for 14 hr. The reaction mixture was treated in the usual ways. Remaining 1-phenyl-tetralone-2, the benzoate of melilotic acid, benzoic acid and melilotic acid were obtained, and the yields were 1.6 g., 12 mg., 0.25 g. and 0.22 g., respectively.

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Intramolecular Interaction between Hydroxyl Group and π-Electrons. II[1]*. Limitation of the Interaction by Chain-length in ω-Hydroxy-1-alkenes**

By Michinori Ōki and Hiizu Iwamura

(Received December 16, 1958)

Recent studies on the intermolecular interaction between the hydroxyl group and aromatic nucleus have led some authors to examine the O–H stretching absorption band in the infrared region with compounds which are considered to possess possible intramolecular interaction between the hydroxyl group and aromatic nucleus. The first of these examples was found by Trifan and his co-workers in α-hydroxyethylferrocene and β-phenylethyl alcohol[2]. However, the phenomenon, splitting of the O–H stretching band, had been known for some years, although those authors who investigated the matter were not quite aware of the cause. That is to say, O–H stretching bands were found by Wulf[3] in 2-hydroxybiphenyl, by Fox and Martin[4] in benzyl alcohol and by Barnard and his collaborators[5] in cumene α-hydroperoxide.

Quite recently Goldman and Crisler[6] have also reported the existence of two O–H stretching bands in the first overtone vibrational region in some β-phenylethyl alcohol derivatives, but these examples mentioned here are all limited to the participation of an aromatic nucleus in the interaction as a hydrogen acceptor. Therefore, the authors felt that it was necessary to know whether a conjugated π-electron system, such as an aromatic ring, is really indispensable to this interaction and carefully investigated the O–H stretching absorption of ω-hydroxy-1-alkenes.

Although the only known example of the intermolecular interaction between the hydroxyl group and isolated double bond was the result of Lüttke and Mecke[7] who found it in cyclohexene and phenol, it turned out to be true that the intramolecular interaction between the hydroxyl group and π-electrons of an isolated double bond does exist, the result being in agreement with that obtained by Baker and Shulgin[8] who published a paper on the interaction in *o*-propenylphenol and *o*-allylphenol during the preparation of this paper.

Experimental

Measurement and Calculation. — The infrared absorption was measured with a Perkin Elmer Model 112-G Double Pass High Precision Grating Infrared Spectrometer[9], the spectral slit width being 1.0 cm^{-1} in the region required. Eastman-Kodak spectro grade or redistilled carbon tetrachloride was used as a solvent. A quartz absorption cell 2 cm. in length was used and the concentration of the solution was 0.0025～0.0032 mol./l. at which dilution the association of the solute is negligible. The temperature was 28.0～28.5°C.

The integrated intensities of the two bands were calculated according to the equations

$$A = \pi/2 \cdot \Delta\nu_{1/2} \cdot \log_e (I_0/I)_{max}$$

$$\log_e (I_0/I) = a/[(\nu-\nu_0)^2+b^2]$$

$$a/b^2 = \log_e (I_0/I)_{max}$$

$$2b = \Delta\nu_{1/2}$$

given by Ramsay[10], where A is the integrated intensity, $\Delta\nu_{1/2}$ the half-width, ν_0 the amount expressed by wave number at the band center and a and b are parameters. Because of the presence of two bands, four parameters had to be used.

Materials.—Allyl alcohol obtained from a commercial source was purified by redistillation using

1) Part I: M. Ōki, H. Iwamura and Y. Urushibara, This Bulletin, **31**, 769 (1958).

* Added in proof: After the submission of this article P. von Schleyer, D. S. Trifan and R. Bacskai have reported in a brief note that they observed two O-H stretching absorptions with allyl alcohol and 3-buten-1-ol [*J. Am. Chem. Soc.*, **80**, 6691 (1958)].

2) D. S. Trifan, J. L. Weinmann and L. P. Kuhn, *J. Am. Chem. Soc.*, **79**, 6566 (1957).

3) O. R. Wulf, ibid., **58**, 2290 (1936).

4) J. J. Fox and A. E. Martin, *Trans. Faraday Soc.*, **36**, 897 (1940).

5) D. Barnard, K. R. Hargrave and G. M. G. Higgins, *J. Chem. Soc.*, **1956**, 2845.

6) I. M. Goldman and R. O. Crisler, *J. Org. Chem.*, **23**, 751 (1958).

7) W. Lüttke and R. Mecke, *Z. Electrochem.*, **53**, 241 (1949).

8) A. W. Baker and A. T. Shulgin, *J. Am. Chem. Soc.*, **80**, 5358 (1958).

9) For calibration of the wave number, see: S. Mizushima et al., *J. Japan. Chem.* (*Kagaku no Ryoiki*), Extra Ed., No. 28, Nankodo, Tokyo (1957) p. 1.

10) D. A. Ramsay, *J. Am. Chem. Soc.*, **74**, 72 (1952).

carbon tetrachloride for removal of water[11], b.p. 96.0~96.3°C. 3-Buten-1-ol and 5-hexen-1-ol were prepared by action of formaldehyde on the corresponding alkenylmagnesium bromides and the physical constants were as follows: 3-buten-1-ol b. p. 113~113.5°C, $n_D^{26.5}$ 1.4185 (lit.[12] b. p. 112~114°, n_D^{25} 1.4189): 5-hexen-1-ol, b.p. 72.0~72.2°C/19.5mm., n_D^{30} 1.4353 (lit.[13] b.p. 155.6~156.0°C/718 mm., n_D^{20} 1.4364). 4-Penten-1-ol and 10-undecen-1-ol were prepared by lithium aluminum hydride reduction of the corresponding carboxylic acids and the following physical constants were obtained: 4-penten-1-ol, b. p. 63°C/3.0 mm., n_D^{21} 1.4292 (lit.[14] $n_D^{?}$ 1.4299); 10-undecen-1-ol, b. p. 95.5~96°C /3.5 mm., n_D^{20} 1.4462 (lit.[15] n_D^{19} 1.4506).

Results and Discussion

The actual O–H stretching absorption curves of the alcohols are shown in Fig. 1 and the data of the two bands divided by the Ramsay's equations are given in Table I, in which, for the convenience of the discussion, the bands are named I and II rather than interacted and free.

As is seen from Fig. 1, the only example which showed two distinct bands is 3-buten-1-ol which can undoubtedly be said to possess intramolecular interaction between the hydroxyl group and π-electrons of the double bond.

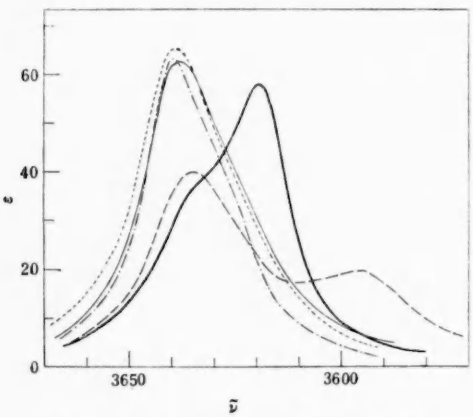

Fig. 1. ν_{O-H} absorption of ω-hydroxy-1-alkenes.
—— allyl alcohol, ---- 3-buten-1-ol,
—— 4-penten-1-ol, ····· 5-hexen-1-ol,
-·-· 10-undecen-1-ol

TABLE I. O–H STRETCHING ABSORPTION BANDS OF ω-HYDROXY-1-ALKENES

$[CH_2=CH(CH_2)_nOH]$

n		ν_{max} (cm^{-1})	$\Delta\nu^{\circ}_{1/2}$ (cm^{-1})	$A\times10^{-4}$ (mol.$^{-1}$·liter·cm^{-2})	$\Delta\nu_{max}$ (cm^{-1})
1	I	3619.4	16.4	2.87	15.4
	II	(3634.8)	(23.4)	(2.29)	
2	I	3596.1	32.2	1.93	39.1
	II	3635.2	24.0	3.27	
3	I	(3624.5)	(24.0)	(1.76)	14
	II	3638.3	20.8	4.03	
4	I	(3626.0)	(17.2)	(1.15)	13
	II	3639.2	20.8	4.45	
9	I	(3628.5)	(18.8)	(1.78)	12
	II	3640.0	15.8	2.94	

The lower homolog of 3-buten-1-ol, allyl alcohol, was spectroscopically studied by Flett[16] in its O–H stretching region and reported to have a single band at 3620 cm^{-1}. However, the present authors' result with the instrument of high resolution shows that allyl alcohol possesses two bands at 3619.4 cm^{-1} and 3634.8 cm^{-1}, the latter corresponding to the normal vibration of aliphatic primary alcohols and is reminiscent of the result obtained by Fox and Martin[4] with benzyl alcohol. Since this kind of curve for O–H stretching vibration is obtained only with allyl alcohol or benzyl alcohol, the band at ca. 3620 cm^{-1} may be attributed to the interaction between π-electrons and the hydroxyl group.

Comparison of the curves for allyl alcohol and 3-buten-1-ol reveals that the number of internally interacted molecules is greater in allyl alcohol than in 3-buten-1-ol, provided that the absorption intensity of a molecule is equal in both free and interacted forms. This assumption is based on the fact that the sum of two integrated intensities is almost the same in the two compounds. This phenomenon seems to be rather striking, because it is a common concept that the difference in wave number corresponds to the energy[17], but can be explained in either of the following two ways. Firstly, the interactions occurring in allyl alcohol and in 3-buten-1-ol may be different in nature and, secondly, unfavorable entropy change in 3-buten-1-ol may limit the number of the internally interacted molecules, in spite of the greater stabilization in energy term. Although, as far as the present data are concerned, it is not clear which is the real cause, the accumulated data

11) O. Kamm and C. S. Marvel, "Org. Synth.", Coll. Vol. I. John Wiley & Sons, Inc., New York (1948), p. 43.
12) E. D. Amstutz, *J. Org. Chem.* **9**, 310 (1944).
13) V. P. Gol'mov, *Zhur. Obshchel Khim.*, **22**, 2132 (1952); *Chem. Abstr.*, **48**, 1240 (1954).
14) M. S. Kharash and C. F. Fuchs, *J. Org. Chem.*, **9**, 359 (1944).
15) P. Chuit, F. Boelsing, J. Hausser and G. Malet, *Helv. Chim. Acta*, **9**, 1074 (1926).
16) M. St. C. Flett, *Spectrochim. Acta*, **10**, 210 (1957).
17) See, e.g., R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, **5**, 839 (1937).

in this laboratory suggest that the former is the preferable cause.

Higher homologs of 3-buten-1-ol, 4-penten-1-ol and 5-hexen-1-ol, possess an unsymmetric band, fatter at the smaller wave number side, and the band can be divided into two, assuming that the band is an overlapping of two symmetric bands which are expressed by the Lorentz function. The smaller peaks (band I) at ca. 3625cm^{-1} may be attributed to the presence of the hydroxyl group and π-electrons interaction but the minor peak (band I) also appears in 10-undecen-1-ol in which the intramolecular interaction is improbable in respect of the entropy increase. Moreover, these three curves are quite similar and suggest that the minor peaks do not represent the intermolecular interaction, since it is not plausible to consider that the same extent of intramolecular interaction between the hydroxyl group and π-electrons exists in these three compounds. In other words, this kind of interaction can not be found in higher homologs than 4-penten-1-ol. The origin of the minor peaks (bands I of 4-penten-1-ol, of 5-hexen-1-ol and of 10-undecen-1-ol) will be dealt with in the following paper.

It may seem to be rather strange that the interaction takes place up to 3-buten-1-ol in the homologs studied, in contrast with the finding of Baker and Shulgin who reported the existence of the interaction both in *o*-propenylphenol and *o*-allylphenol, the latter being an analog of 4-penten-1-ol. But the explanation can be given by considering the difference in proton donating ability of phenolic and alcoholic hydroxyl groups and the favorable structure of the phenols in which O–C–C–C bonds are fixed *cis*. The representative cases are under investigation.

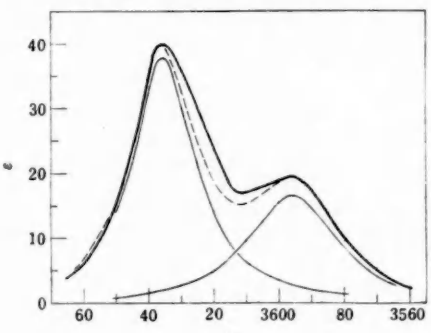

Fig. 2. ν_{O-H} absorption of 3-buten-1-ol.
— observed curve
—— divided bands
---- calculated curve

It might also be mentioned here that, as shown in Fg. 2, the calculated band area of 3-buten-1-ol does not quite agree with the observed one. Namely, the computed value is always lower than the observed one at the valley of the band for 3-buten-1-ol, while that for the others

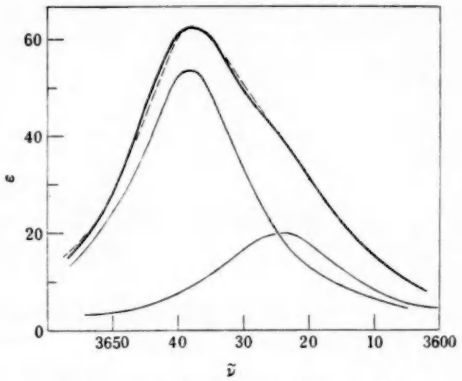

Fig. 3. ν_{O-H} absorption of 4-penten-1-ol.
— observed curve
—— divided bands
---- calculated curve

agree, as shown in Fig. 3 (taking 4-penten-1-ol as an example). The cause of the disagreement is unknown but is quite understandable if one considers that another absorption band exists in this compound at about 3626 cm^{-1} corresponding to those in the higher homologs.

In closing, the authors would like to mention the terminology of this interaction. Although many authors[2,6,8] used "hydrogen bonding", "interaction" is the present authors' choice, since the definition of the hydrogen bonding was discussed at the international symposium[18] on the hydrogen bonding and an agreement that the interaction between a hydrogen donating group and an electron pair of an atom was hydrogen bonding, was reached. The interaction discussed here undoubtedly resembles the hydrogen bonding, but is still distinguishable from the hydrogen bonding because of the participation of the π-electrons of a double bond which are not on the same atom, although they overlap.

Summary

Infrared absorption was measured with

18) See: *Angew. Chem.*, **67**, 755 (1957).

five ω-hydroxy-1-alkenes in the 3 μ region, using an instrument of high resolution and the following results were obtained.

1) Intramolecular interaction between the hydroxyl group and π-electrons was found in allyl alcohol and in 3-buten-1-ol.

2) Interactions which occur in allyl alcohol and in 3-buten-1-ol may be of a different kind.

3) Higher homologs also possess two O–H stretching absorption bands but these bands can not be associated with the intramolecular interaction.

The authors are indebted to Professors Y. Urushibara and T. Shimanouchi for their valuable advice and encouragement and to Mr. I. Suzuki for his technical assistance throughout this work. A part of the cost was defrayed from the Grant in Aid for Fundamental Scientific Research of the Ministry of Education, for which the authors' thanks are due.

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Analysis of the Multi-azeotropes in Terms of the Zeroth Approximation

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(Received October 3, 1958)

Theoretical and experimental studies on the binary azeotropes, characterized by a maximum or a minimum in vapor pressure curves, have been made by many investigators. Among them, the theoretical studies of Prigogine[1], Mashiko[2] and Ikari[3], in terms of strictly regular solutions are viewed with interest.

However, most of these studies have dealt only with the case of binary systems. We shall report here the results obtained in the theoretical study of multi-azeotropes in the zeroth approximation by extending the method of Prigogine and Mashiko.

Theoretical Equation of the Vapor-liquid Equilibrium in Terms of the Zeroth Approximation.—The authors[4] have already published the theoretical equations of the vapor-liquid equilibrium in multi-component systems at the zeroth approximation.

Rewriting, now, the final result of activity coefficient γ_i of i-th component, the following equation is given

$$\boldsymbol{R}T\ln\gamma_i = \sum_{p=1}^{n}(1-x_i)x_p\omega_{ip}(i\neq p) - \sum_{p,q=1}^{n} x_p x_q \omega_{pq}\left(\begin{matrix}p\neq q\\ p,q\neq i\end{matrix}\right) \qquad (1)$$

where x is mole fraction of component of subscription $1,2,\cdots\cdots,i,\cdots\cdots,n$ in liquid phase, ω the inter-molecular exchange energy in different molecules, $\boldsymbol{R}$ the gas constant and T the absolute temperature in the equilibrium state.

Taking as an example the case of a binary solution, Eq. 1 becomes as follows:

$$\begin{cases}\boldsymbol{R}T\ln\gamma_1 = (1-x_1)x_2\omega_{12}\\ \boldsymbol{R}T\ln\gamma_2 = (1-x_2)x_1\omega_{12}\end{cases} \qquad (2)$$

which is the same as given by Guggenheim[5].

Condition of the Azeotropic Formation in Multi-component System.—The activity coefficient of the i-th component in liquid phase is given by

$$\gamma_i = \pi y_i/p_i^\circ x_i \qquad (3)$$

where π is the total pressure, y the mole fraction in vapor phase and p° the vapor pressure of pure component at temperature T.

At an azeotropic point, $y_i = x_i$ and by the Clausius-Clapeyron's equation, $\ln\gamma_i$ is expressed as

$$\boldsymbol{R}\ln\gamma_i = \Delta H_i(1/T - 1/T_i^\circ) \qquad (4)$$

where ΔH is the heat of vaporization of

1) I. Prigogine and R. Defay, "Chemical Thermodynamics", Translated by D. H. Everett, Longmans, London, (1954), p. 450.

2) Y. Mashiko, *Rep. Gov. Chem. Ind. Res. Inst. Tokyo*, **52**, 158 (1957).

3) A. Ikari, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **60**, 1375 (1957).

4) I. Yamada, will be published in *Chem. Eng. Japan*.

5) E. A. Guggenheim, "Mixtures", Oxford University Press (1952), p. 32.

TABLE I. EXAMPLES OF AZEOTROPIC RELATIONS IN TERNARY AZEOTROPES

Components of system	Boiling point (B. P.)	B. P. difference	$\omega_{ij}/\Delta S_i$	$\omega_{ij}/\Delta S_j$	Azeotropes
Ethanol (1)		$\Delta_{12}=$ 2.2	69.4	53.6	
—Cyclohexane (2)	62.1°C	$\Delta_{32}=$ 19.2	97.4	115.9	exist
—Water (3)		$\Delta_{13}=-21.4$	26.0	28.2	
iso-Propanol (1)		$\Delta_{12}=-$ 1.2	68.7	50.7	
—Cyclohexane (2)	63.8°C	$\Delta_{32}=$ 19.2	93.5	111.3	exist
—Water (3)		$\Delta_{13}=-17.5$	37.3	42.4	
Allylalcohol (1)		$\Delta_{12}=-16.3$	94.7	73.0	
—Cyclohexane (2)	65.2°C	$\Delta_{32}=$ 19.2	90.0	107.2	exist
—Water (3)		$\Delta_{13}=-$ 2.9	25.1	27.4	
Ethanol (1)		$\Delta_{12}=$ 1.8	55.4	71.5	
—Benzene (2)	64.8°C	$\Delta_{32}=$ 19.8	106.9	129.8	exist
—Water (3)		$\Delta_{13}=-21.6$	49.8	53.0	
iso-Propanol (1)		$\Delta_{12}=-$ 1.7	65.7	48.5	
—Benzene (2)	65.3°C	$\Delta_{32}=$ 19.7	89.7	104.6	exist
—Water (3)		$\Delta_{13}=-18.5$	31.6	27.8	
Allylalcohol (1)		$\Delta_{12}=-17.3$	109.1	79·6	
—Benzene (2)	67.8°C	$\Delta_{32}=$ 19.8	85.6	101.8	exist
—Water (3)		$\Delta_{13}=-$ 2.5	42.7	42.7	
Methanol (1)		$\Delta_{12}=$ 8.2	−6.1	−6.9	
—Acetone (2)	61.7°C	$\Delta_{32}=$ 35.3	31.2	31.1	none-exist
—Water (3)		$\Delta_{13}=-43.5$	64.8	57.6	

B. P. shows the azeotropic point under 1 atm.

pure component and T° is the boiling point under the pressure π.

From Eqs. 1 and 4, the following expressions for the i- and j-th components can be deduced by substituting ΔS for $\Delta H/T$

$$\Delta S_i(T_i^\circ - T) = \sum_{p=1}^{n}(1-x_i)x_p\omega_{ip}(i\neq p) - \sum_{p.q=1}^{n} x_p x_q \omega_{pq}\begin{pmatrix} p\neq q \\ p.q\neq i\end{pmatrix} \quad (5)$$

$$\Delta S_j(T_j^\circ - T) = \sum_{p=1}^{n}(1-x_j)x_p\omega_{jp}(j\neq p) - \sum_{p.q=1}^{n} x_p x_q \omega_{pq}\begin{pmatrix} p\neq q \\ p.q\neq j\end{pmatrix} \quad (6)$$

and

$$T_i^\circ - T_j^\circ = \left\{\sum_{p=1}^{n}(1-x_i)x_p\omega_{ip}(i\neq p) - \sum_{p.q=1}^{n} x_p x_q \omega_{pq}\begin{pmatrix} p\neq q \\ p.q\neq i\end{pmatrix}\right\}\Delta S_i^{-1} - \left\{\sum_{p=1}^{n}(1-x_j)x_p\omega_{jp}(j\neq p) - \sum_{p.q=1}^{n} x_p x_q \omega_{pq}\begin{pmatrix} p\neq q \\ p.q\neq j\end{pmatrix}\right\}\Delta S_j^{-1} \quad (7)$$

When $x_j=1$, Eq. 7 shows a maximum and when $x_i=1$, a minimum, so that the following relation should hold.

$$-\omega_{ij}/\Delta S_j \leqq T_i^\circ - T_j^\circ \leqq \omega_{ij}/\Delta S_i \quad (8)$$

Hence, in the case of multi-azeotropes, the same relation as Eq. 7 should hold for all such combinations made of n components.

In the case of binary azeotropes, Eq. 8 takes the form given by Mashiko[6]. Table I shows the azeotropic relations from the given data[7], and the values of ω_{ij} are calculated from Eq. 1 for ternary systems.

Constancy of ω_{ij}.—The theoretical equations of the vapor-liquid equilibrium in multicomponent systems on the zeroth approximation have been derived by assuming that the molecular configurations have pairs in the liquid phase and intermolecular exchange energy between molecules i and j are independent of each other. If these assumptions are correct ω_{ij} should have a constant value for any pair of components.

ω_{ij} can be obtained by solving Eq. 1 for a given set of values of T, x_i and γ_i, i being $1, 2, \cdots\cdots, n$.

In the case of ternary azeotropes, the following solution can be obtained

$$\omega_{12}\Delta = \boldsymbol{M}$$

where

6) M. Mashiko, *Rep. Gov. Chem. Ind. Res. Inst. Tokyo*, **52**, 160 (1957).

7) L. H. Horsley, *Anal. Chem.*, **19**, 508 (1947); **21**, 831 (1949).

$$\Delta = \begin{bmatrix} (1-x_1)x_2 & -x_2x_3 & (1-x_1)x_3 \\ (1-x_2)x_1 & (1-x_2)x_3 & -x_1x_3 \\ -x_1x_2 & (1-x_3)x_2 & (1-x_3)x_1 \end{bmatrix}$$

and

$$\boldsymbol{M} = \begin{bmatrix} \Delta H_1(1-T/T_1^\circ) & -x_2x_3 & (1-x_1)x_3 \\ \Delta H_2(1-T/T_2^\circ) & (1-x_2)x_3 & -x_1x_3 \\ \Delta H_3(1-T/T_3^\circ) & (1-x_3)x_2 & (1-x_3)x_1 \end{bmatrix}$$

By plotting Δ vs. $\boldsymbol{M}$, a linear relation is obtained for several ternary systems as shown in Figs. 1—3.

Temperature Effect upon Azeotropic Compositions.—Taking the difference between $\ln\gamma_i$ and $\ln\gamma_{i+1}$ for all i's in Eq. 1, all second order terms $x_px_q\omega_{pq}$ cancel each other and the following equation can be obtained.

$$\Delta H_i(1-T/T_i^\circ) - \Delta H_{i+1}(1-T/T_{i+1}^\circ) = (x_{i+1}-x_i)\omega_{i\,i+1} + \sum_{p=1}^{n}(\omega_{ip}-\omega_{j+p})x_p \qquad (p \neq i, i+1) \quad (12)$$

where $i = 1, 2, \cdots\cdots, n-1$

As $\sum x = 1$, Eq. 12 becomes

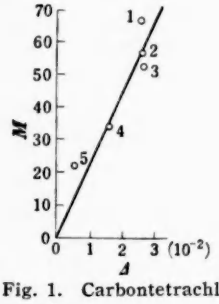
$$\begin{bmatrix} 1 \\ \Delta\phi_{1\,2} \\ \vdots \\ \Delta\phi_{i\,j+1} \\ \vdots \\ \Delta\phi_{n-1,n} \end{bmatrix} = \begin{bmatrix} 1 & 1 & \cdots\cdots & 1 & 1 & \cdots\cdots & 1 \\ -\omega_{1\,2} & \omega_{1\,2} & \cdots\cdots & (\omega_{1\,i}-\omega_{2\,i}) & (\omega_{1\,i+1}-\omega_{2\,i+1}) & \cdots\cdots & \\ (\omega_{1\,i}-\omega_{1\,i+1}) & (\omega_{2\,i}-\omega_{2\,i+1}) & \cdots\cdots & -\omega_{i\,i+1} & \omega_{i\,i+1} & \cdots\cdots & (\omega_{i\,n}-\omega_{i+1\,n}) \\ (\omega_{1\,n-1}-\omega_{1\,n}) & (\omega_{2\,n-1}-\omega_{2\,n}) & \cdots\cdots & (\omega_{i\,n-1}-\omega_{i\,n}) & (\omega_{i+1\,n-1}-\omega_{i+1\,n}) & \cdots\cdots & \omega_{n-1\,n} \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ \vdots \\ x_i \\ \vdots \\ x_n \end{bmatrix} \qquad (13)$$

where

$$\Delta\phi_{i\,i+1} = \Delta H_i(1-T/T_i^\circ) - \Delta H_{i+1}(1-T/T_{i+1}^\circ)$$

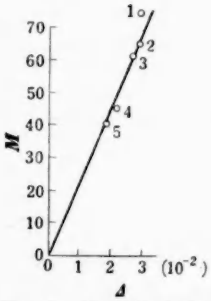
Consequently, x's can be expressed by linear functions of T for given values ω_{ij}'s, ΔH_i's and T_i°'s.

For binary azeotropes, the following results can be given.



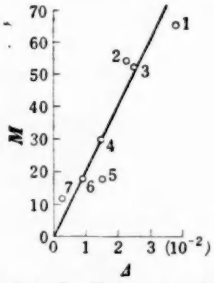
Alcohols
1 ethanol
2 *t*-butanol
3 propanol
4 allyl alcohol
5 *sec*-butanol

Fig. 1. Carbontetrachloride-water-alcohol system.



Alcohols
1 ethanol
2 *iso*-propanol
3 *t*-butanol
4 allyl alcohol
5 propanol

Fig. 2. Cyclohexane-water-alcohol system.



Alcohols
1 ethanol
2 *iso*-propanol
3 *t*-butanol
4 propanol
5 allyl alcohol
6 *sec*-butanol
7 hexanol

Fig. 3. Benzene-water-alcohol system.

$$\begin{bmatrix} 1 \\ \Delta H_1(1-T/T_1^\circ) - \Delta H_2(1-T/T_2^\circ) \end{bmatrix} = \begin{bmatrix} 1 & 1 \\ -\omega & \omega \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \end{bmatrix} \qquad (14)$$

Consequently

$$2x_1 = 1 - \{\Delta H_1(1-T/T_1^\circ) - \Delta H_2(1-T/T_2^\circ)\}\omega^{-1} \qquad (15)$$

$$2x_2 = 1 + \{\Delta H_1(1-T/T_2^\circ) - \Delta H_2(1-T/T_2^\circ)\}\omega^{-1} \qquad (16)$$

Eqs. 15 and 16 agree with those given by Prigogine[8].

Breaking Point of Azeotropes.—When x_i obtained by solving Eq. 13 is equal to zero or unity, the multi-azeotropes are broken; these points are predicted by solving the equation for $i = 1, 2, \cdots\cdots, n$.

8) I. Prigogine and R. Defay, "Chemical Thermodynamics", Translated by D. H. Everett, Longmans, London, (1954), p. 462.

The closest value to initial T obtained for each may be considered as the break point.

Prediction of Azeotropic Temperature.— Substituting Eq. 4 and x_i given by Eq. 13 into Eq. 1, the azeotropic temperature can be predicted by solving the second-order equation in respect to T for given values of ω_{ii}, T_i°, ΔH and R.

Summary

Assuming the zeroth approximation for the vapor-liquid equilibrium in multi-component systems the authors have analyzed multi-azeotropes, and the following results have been obtained.

1) For the condition of azeotropic formation in multi-component systems, Eq. 8 should hold for all combinations of n components.

2) The constancy of ω_{ij} is shown as Figs. 1 to 3.

3) Azeotropic composition effect upon temperature is given by solving Eq. 13, and the breaking temperatures are obtained by substituting $x_i=1$ or 0 into Eq. 13.

4) Azeotropic temperature can be deduced from Eqs. 2, 4 and 13.

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Polarography of Tetracyano- and Dithiooxalato-Nickelate(II) Complexes[1]

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(Received October 10, 1958)

There have been no reports on the polarographic reduction of dithiooxalato-nickelate(II) complex, although some studies have been reported for tetracyano-nickelate(II) complex by several authors[2-8]. For instance, Hume et al.[6] studied the polarographic behavior of the tetracyanonickelate(II) ion and found that the ion, $[Ni(CN)_4]^{2-}$, is irreversibly reduced in one step and the wave corresponds to a two-electron reduction of the ion to metal. They also found that the univalent nickel complex ion, $[Ni_2(CN)_6]^{4-}$, is oxidized, but not reduced polarographically.

Recently, Vlček[7,8] studied the mechanism of the electrochemical reduction of the ion, $[Ni(CN)_4]^{2-}$, in further detail and obtained the following results. The electrochemical reduction of the ion, $[Ni(CN)_4]^{2-}$, proceeds principally by the acceptance of two electrons. The reduction product of the two-electron reduction may be either metallic nickel or a complex of zero-valent nickel, $[Ni(CN)_4]^{4-}$, the latter of which is very unstable in solution and is immediately oxidized to univalent nickel with evolution of hydrogen and simultaneous formation of the deep red ion, $[Ni_2(CN)_6]^{4-}$.

$$2[Ni(CN)_4]^{4-}+2H_2O = [Ni_2(CN)_6]^{4-}+2CN^-+2OH^-+H_2$$

The ion, $[Ni_2(CN)_6]^{4-}$, is also oxidized to $[Ni(CN)_4]^{2-}$, though the rate is very small. The increase of the current in solution with a high concentration of the cyanide ion was explained as being due to the regeneration of bivalent nickel from the product of the electrode reaction.

The present paper deals with the polarography of the tetracyano- and dithiooxalato-nickelate(II) ions. The main purpose of this study is to examine polarographically whether the mixed complex is formed or not in the solution when the two kinds of ion, $[Ni(CN)_4]^{2-}$ and $[Ni(C_2S_2O_2)_2]^{2-}$, were mixed together.

1) Partly presented at the Symposium on Co-ordination Compounds, Tokyo, November 15, 1958.

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2) N. V. Emelianova, *Rec. trav. chim.*, **44**, 529 (1925).

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4) J. P. Hochstein, *J. Gen. Chem. U. S. S. R.*, **7**, 2488 (1937).

5) V. Caglioti, G. Sartori and P. Silvestroni, *Atti accad. natl. Lincei, Classe Sci. fis. mat. nat.*, **3**, 448 (1947).

6) D. N. Hume and I. M. Kolthoff, *J. Am. Chem. Soc.*, **72**, 4423 (1950).

7) A. A. Vlček, *Collection Czechoslov. Chem. Communs.*, **22**, 948 (1957).

8) A. A. Vlček, ibid., **22**, 1736 (1957).

Experimental

Apparatus.—A Yanagimoto model 104 polarograph with a sensitivity of galvanometer (2×10^{-9} μA/mm./m.) was used. For the determination of the half-wave potentials, the method previously described was employed[9]. An H-type cell with a saturated calomel electrode was used. The capillary used had a rate of flow of mercury, 0.635 mg./sec., and a drop time of 4.16 sec. in the solution of 1 F potassium chloride at an open circuit with a mercury head of 66.5 cm. The capillary was connected with a mercury reservoir by a tube of polyvinyl chloride. All the measurements were made at 28±0.1°C, the temperature being maintained by a water thermostat. The reversibilities of the electrode reactions were tested by determining the slope of $\log i/(i_d-i)$ vs. potential. Slopes of the log plots indicated irreversible reduction throughout.

Material. — The complex compounds studied were prepared by the following methods.

1. *Tetracyanonickelate(II) complx*, $K_2[Ni(CN_4]\cdot H_2O$. — Pure potassium tetracyanonickelate(II) complex was prepared in the usual way by dissolving freshly precipitated nickel cyanide in potassium cyanide and evaporating the filtered solution. On recrystallization from hot water, an orange crystalline product was obtained.

2. *Dithiooxalatonickelate(II) complex*, $K_2[Ni\cdot(C_2S_2O_2)_2]$[10,11]. — Concentrated aqueous solutions of nickel sulfate (2 g. in 10 ml.) and potassium dithiooxalate (2 g. in 4 ml.) were mixed at room temperature; a deep purple solution was at once produced, from which small, almost black crystals separated. The product prepared in this way is contaminated by the remaining simple salt and may be purified by recrystallization from hot water. After dissolving the crystals in water at 40°C, one-half its volume of the saturated solution of potassium nitrate was added to the solution, from which the large iridescent bipyramidal crystals separated again on cooling. The crystals were filtered and washed several times with water and ethanol; then they were transferred to a vacuum desiccator to remove the remaining ethanol.

The complex compounds used were checked for purity by the comparison of the ultraviolet absorption spectra. Each solution for electrolysis was made freshly from the dry crystalline nickelate-(II) complexes before use. The solutions were mainly 0.005 F or 0.01 F with respect to the complex ion studied. In order to remove the dissolved oxygen, a vigorous stream of nitrogen which was purified from oxygen by means of an alkaline solution of pyrogallol was passed through the cell solution for an hour prior to each electrolysis, preventing the evaporation.

In order to examine the formation of the mixed complex, two kinds of solution of the same concentration for each ion were mixed together after the removal of the dissolved oxygen. After mixing, a stream of nitrogen was passed further for about ten minutes. Each polarographic run was completed within ten minutes. The maximum suppressor, Tween-80**, was added to the solution, which was enough to suppress the maxima of both the waves of the ions, $[Ni(CN)_4]^{2-}$ and $[Ni(C_2S_2O_2)_2]^{2-}$. (0.0032% Tween-80). The supporting electrolyte used was 1 F potassium chloride.

9) N. Maki, Y. Shimura and R. Tsuchida, This Bulletin, **30**, 909 (1957).
10) H. O. Jones and H. S. Tasker, *J. Chem. Soc.*, **95**, 1904 (1909).
11) E. G. Cox, W. Wardlaw and K. C. Webster, ibid., **1935**, 1475 (1935).

Results and Discussion

The dithiooxalatonickelate(II) complex ion, $[Ni(C_2S_2O_2)_2]^{2-}$, is reduced irreversibly in two steps at the dropping mercury electrode in the solution of 1 F potassium chloride, as is shown in Fig. 1. The waves have a maximum at around −1.1 V. (vs. S. C. E.), which could easily be suppressed in the presence of 0.0032% Tween-80. The ratio of the height of the first wave to that of the second is approximately 1:1. This ratio is independent

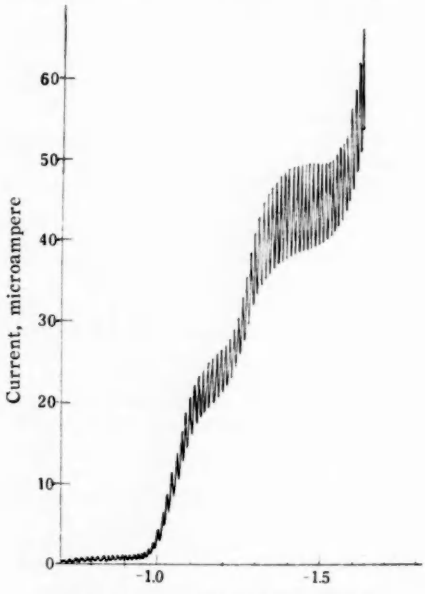


Fig. 1. The polarogram of $[Ni(C_2S_2O_2)]^{2-}$ obtained at the concentration of 0.005 F in the presence of 0.0032% Tween-80. Supporting electrolyte; 1 F KCl. Temp., 28°C. Sensitivity; 0.400 μA/mm., Damping; 200. $E_{1/2}$ of 1st wave = −1.03 V., $E_{1/2}$ of 2nd wave = −1.25 V. vs. S. C. E.

** Polyoxyethylene sorbitan mono-oleate (Atlas Powder Co., in U. S. A.).

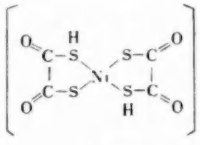
TABLE I. THE HALF-WAVE POTENTIALS AND THE CURRENT VALUES OF THE WAVES OF DITHIOOXALATONICKELATE(II) ION, $[Ni(C_2S_2O_2)_2]^{2-}$

Concn. of the ion (F)	$E_{1/2}$ of the 1st wave (V.)	$E_{1/2}$ of the 2nd wave (V.)	Total height of the waves (μA)
10^{-2}	−1.03	−1.25	80.0
5×10^{-3}	−1.03	−1.25	41.0
10^{-3}	−1.10	−1.31	20·8

1) The data obtained in the presence of 0.0032% Tween-80.
2) Supporting electrolyte; 1 F KCl.
3) Potential unit; V. vs. S. C. E., Temp., 28°C.
4) Characteristics of the capillary used; $m=0.635$ mg./sec., $t=4.16$ sec.

of the concentration of the complex ion. The limiting current for the unit concentration of the ion, i_l/c, becomes greater with the decreasing concentration of the ion. Table I shows the relation between the current value and the concentration. The fact that the heights of the waves of dithiooxalato complex are significantly greater than those of the usual nickel(II) complexes, such as $[Ni(CN)_4]^{2-}$, may well be explained as being due to the following reason. Namely, a part of the dithiooxalato complexes is considered to be present in solution as a form of the complex having protons to the sulfur atom.

For instance;



Hence, at the reduction potential of the complex, the hydrogen ion liberated from the complex is coreduced and contributes to the limiting current of the nickelate(II) complex. In conjunction with this consideration, the fact that the ratio of the height of the first wave to that of the second is always approximately 1:1 supports the idea that the dithiooxalatonickelate(II) complex might perhaps be reduced to the nickel(0) state in two steps. However, it appears desirable to delay further speculation on possible mechanisms of the reduction until more evidence, such as the data in buffer solution, is available. Concerning this point, further study is to be carried out in more detail and to be reported later.

On the other hand, the tetracyanonickelate(II) ion, $[Ni(CN)_4]^{2-}$, is reduced irreversibly in one step at the dropping mercury electrode in 1 F potassium chloride supporting electrolyte. (Fig. 2). The height of the wave is roughly proportional to the concentration of the complex ion. According to the results obtained by Vlček[7,8] and Hume et al.[6], the wave, corresponding to a gain of two electrons, represents the reduction for nickel(II) to nickel(0). In the solution of 1 F potassium chloride the wave of this ion indicated the maximum, which could be suppressed in the presence of 0.0016% Tween-80. In the solution of 0.5 F potassium sulfate it was very difficult to diminish the oxygen waves, which appeared at around −0.55 and −0.85 V. (vs. S. C. E.). Accordingly, the solution of 1 F potassium chloride was used as a supporting electrolyte to examine the formation of the mixed complex.

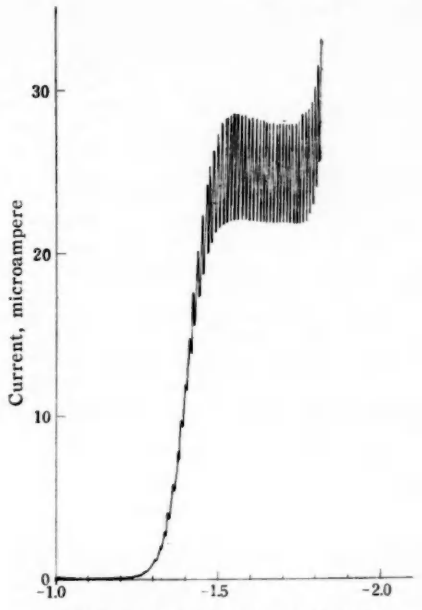


Fig. 2. The polarogram of $[Ni(CN)_4]^{2-}$ obtained in the solution of 1 F KCl at the concentration of 0.005 F in the presence of 0.0016% Tween-80. Sensitivity; 0.200 μA/mm., Damping; 200. $E_{1/2}=-1.38_5$ V. vs. S. C. E. $i_d=25.3$ μA.

In order to confirm the formation of the mixed complex, the solution of tetracyanonickelate(II) ion, $[Ni(CN)_4]^{2-}$, and of dithiooxalatonickelate(II) ion, $[Ni(C_2S_2O_2)_2]^{2-}$, are mixed together at each concentration of 10^{-2} F in the presence of

0.0032% Tween-80 after the removal of the dissolved oxygen. The polarogram of the mixed solution was taken within about a quarter of an hour after mixing. If the reaction between the complex ions, $[Ni(CN)_4]^{2-}$ and $[Ni(C_2S_2O_2)_2]^{2-}$, takes place, it is expected that the new reduction wave of the mixed complex ion, $[Ni(C_2S_2O_2)(CN)_2]^{2-}$, is obtained. This is neither the wave of the ion, $[Ni(CN)_4]^{2-}$, nor that of the ion, $[Ni(C_2S_2O_2)_2]^{2-}$. In fact, both the waves of the original ions, $[Ni(CN)_4]^{2-}$ and $[Ni(C_2S_2O_2)_2]^{2-}$, almost disappeared and a new well-defined wave was obtained near the potential between the waves of the original ions. This fact may be regarded as a proof for the formation of the mixed complex ion, $[Ni(C_2S_2O_2)(CN)_2]^{2-}$, in the solution. (Fig. 3).

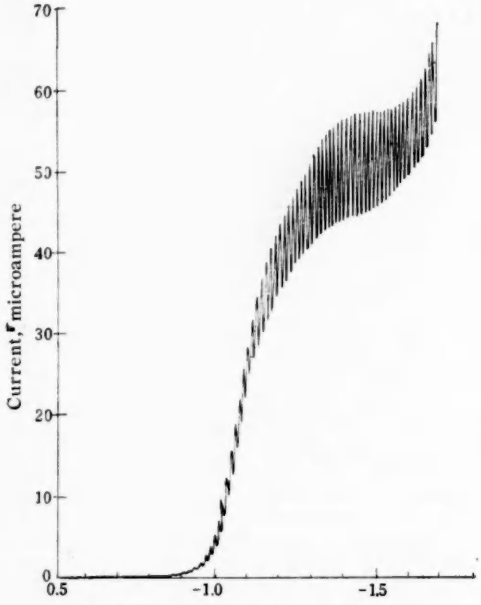
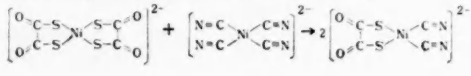


Fig. 3. The polarogram of the mixture of $[Ni(CN)_4]^{2-}$ and of $[Ni(C_2S_2O_2)_2]^{2-}$ at the equal concentration of 0.01 F for each complex ion obtained in the presence of 0.0032% Tween 80. The supporting electrolyte; 1 F KCl. $E_{1/2}$ of the wave $=-1.06$ V. vs. S. C. E. $i=47.6$ μA. Sensitivity; 0.400 μA/mm., Damping; 200.

It is considered that the reaction proceeds by the following equation;



The reaction was so fast that the progress of the reaction could not be detected nor traced by the classical polarographic method. The results obtained here are also supported by those of the spectrochemical study obtained by Kida[12].

The mixed complex ion, $[Ni(C_2S_2O_2)\cdot(CN)_2]^{2-}$, gives the irreversible wave of one step in the presence of 0.0032% Tween-80 in the solution of 1 F potassium chloride. The current is roughly proportional to the square root of the height of the mercury column. The straight line plot, however, does not pass through the origin but gives a negative intercept on the current axis. The height of the wave was not proportional to the concentration of the original ions. The half-wave potential of the wave shifts to the positive direction of potential with the decreasing concentration of the original ions.

For the same purpose as in the case of the dithiooxalatodicyanonickelate(II) complex, the polarogram of the mixed solution of the ions, $[Cu\,en_2^{***}]^{2+}$ and $[Cu\,ox_2^{***}]^{2-}$, was taken at equal concentration of both

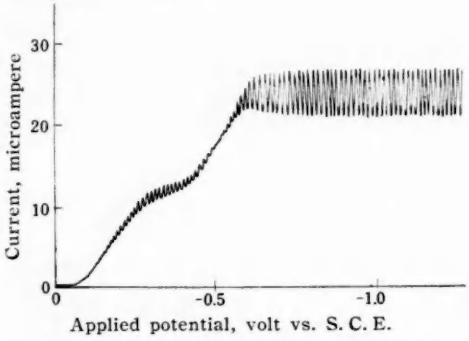


Fig. 4. The polarogram of the mixed solution of $[Cu\,ox_2]^{2-}$ and $[Cu\,en_2]^{2+}$ obtained in the presence of 0.0032% Tween-80. The supporting electrolyte used is 0.5 F $NaClO_4$. The mixed solution was prepared by mixing the solution of the same amount of $[Cu\,ox_2]^{2-}$ and of $[Cu\,en_2]^{2+}$ at each concentration of 0.005 F at 25°C. The half-wave potentials of both the waves were quite the same as those of the original ions, $[Cu\,ox_2]^{2-}$ and $[Cu\,en_2]^{2+}$.
$E_{1/2}$ of $[Cu\,ox_2]^{2-} = -0.14_5$ V. vs. S.C.E.
$E_{1/2}$ of $[Cu\,en_2]^{2+} = -0.49$ V. vs. S.C.E.
While the height of the wave becomes one half, since one is diluted to double by another.

12) S. Kida, This Bulletin, **29**, 805 (1956).
*** The following abbreviation was used; en=ethylenediamine, ox=oxalate.

the ions in the presence of 0.0032% Tween-80. (Fig. 4). In this case, however, the reduction waves obtained were only those of the original ions, $[Cu\,en_2]^{2+}$ and $[Cu\,ox_2]^{2-}$, and the wave of the mixed complex, [Cu en ox], could not be found, though the presence of this was verified by Kida[12] and DeWitt et al.[13] Namely, the percentage of the mixed complex formed in the solution is calculated to be 64%**** when equal amounts of both the ions, $[Cu\,en_2]^{2+}$ and $[Cu\,ox_2]^{2-}$, were mixed together at room temperature. This fact is explained as being due to the presence of the fast equilibrium among these complexes, $[Cu\,en_2]^{2+}$, $[Cu\,ox_2]^{2-}$ and [Cu en ox]. In other words, at the reduction potential of the ions, $[Cu\,en_2]^{2+}$ and $[Cu\,ox_2]^{2-}$, the equilibrium shifts very fast to the direction for supplying these ions. Further, in the equilibrium of the system,

$$[Ni(C_2S_2O_2)_2]^{2-} + [Ni(CN)_4]^{2-} \rightleftarrows 2[Ni(C_2S_2O_2)(CN)_2]^{2-}$$

its rate is very small. Consequently, the reduction wave of the mixed complex can be found. This fact suggests that the coordinating bond of these complexes has a considerable covalent character, in spite of the fact that the exchange reaction of tetracyanonickelate(II) ion with radioactive cyanide in solution is very fast[14].

13) R. DeWitt and J. Watters, *J. Am. Chem. Soc.*, **76**, 3810 (1954).
14) F. A. Long, ibid., **73**, 537 (1951).
**** The influence of temperature on the percentage is considered to be small.

Summary

1. It was verified polarographically that the reaction between the ions, $[Ni(CN)_4]^{2-}$ and $[Ni(C_2S_2O_2)_2]^{2-}$, takes place and the mixed complex ion, $[Ni(C_2S_2O_2)(CN)_2]^{2-}$, is formed in solution. The rate of the reaction was so great that the progress of the reaction could not be traced by the usual polarographic method. Meanwhile the wave of the oxalato-ethylenediamine copper(II) complex, [Cu en ox], the presence of which in solution had been verified spectrophotometrically, was not detected polarographically. That is to say, the polarographic method can be applied to detect the formation of the mixed complex, the coordinating bonds of which have a considerable covalent character, such as $[Ni(C_2S_2O_2)(CN)_2]^{2-}$, but can not be applied to detect the mixed complex having ionic bonds.

2. The ion, $[Ni(C_2S_2O_2)_2]^{2-}$, is reduced irreversibly in two steps at the dropping mercury electrode in the presence of 0.0032% Tween-80, when 1 F potassium chloride solution was used as a supporting electrolyte. The heights of the two waves are not proportional to the concentration of the ion. The height of the wave for the unit concentration of the ion increases with the decreasing concentration of the ion.

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The Kinetics of the Complex-forming Reaction between Nickel(II) and Ethylenediaminetetraacetate

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Although there are a number of papers concerning the inorganic reactions involving metal complexes, few of them deal with the kinetics of the complex-forming reactions between metal ions and organic ligands. Several investigations in which the dissociation reactions, the substitution reactions or the exchange reactions involving metal-ethylenediaminetetraacetate complexes were dealt with have given some information of the complex-forming reactions between the metal and ethylenediaminetetraacetate (EDTA)[1-5]. Those reactions, which are reactions of copper(II)[3], cadmium II)[2], lead(II)[5], nickel (II)[4], and iron(II)[1] with EDTA, proceed so rapidly that the direct measurement of the concentration-time relation by the conventional techniques seems to be difficult.

Recently, a rotated dropping mercury electrode (RDME) has been developed, which has a current sensitivity some ten times as great as that of the conventional dropping mercury electrode[6-12]. In this investigation, the rate of the complex-forming reaction between nickel(II) and EDTA was followed by measuring the limiting current of nickel(II) at the RDME. The mechanisms of the reaction and the rate constant for each reaction path are presented in this paper.

Theoretical

Let us consider a complex-forming reaction of nickel(II) with ethylenediaminetetraacetate (EDTA) in sodium acetate-acetic acid buffers which contain 0.1 M acetate. At pH of the acetate buffer, EDTA exists mainly in the form of H_2Y^{2-} and partly in the forms of H_3Y^- and HY^{3-}, where Y^{4-} denotes the completely dissociated EDTA anion. These species are in equilibrium given in Eqs. 1 and 2.

$$H_3Y^- \rightleftarrows H_2Y^{2-} + H^+ \quad (1)$$

$$H_2Y^{2-} \rightleftarrows HY^{3-} + H^+ \quad (2)$$

Nickel(II) forms acetato complexes in a solution containing acetate ions. It has been found that the monoacetatonickel(II) ion is a predominant species of acetato complexes unless the concentration of acetate exceeds 0.2 M[13]. The monoacetatonickel(II) and the hydrated nickel ions are in equilibrium according to the equation,

$$Ni^{2+} + OAc^- \rightleftarrows NiOAc^+ \quad (3)$$

The reaction between nickel(II) and EDTA may proceed through various reaction paths. Among three ionic species of EDTA mentioned above, H_3Y^- is considered to be the least favorable to react with nickel(II). The rate of the reaction between nickel(II) and H_3Y^- seems to be much smaller than those between nickel (II) and other ionic species of EDTA. From these considerations, the following reaction paths are assumed:

$$Ni^{2+} + HY^{3-} \xrightarrow{k_{1a}} NiHY^- \quad (4)$$
$$NiHY^- \rightleftarrows NiY^{2-} + H^+$$

$$Ni^{2+} + H_2Y^{2-} \xrightarrow{k_{2a}} NiH_2Y \quad (5)$$
$$NiH_2Y \rightleftarrows NiHY^- + H^+ \rightleftarrows NiY^{2-} + 2H^+$$

$$NiOAc^+ + HY^{3-} \xrightarrow{k_{1b}} NiHY^- + OAc^- \quad (6)$$
$$NiHY^- \rightleftarrows NiY^{2-} + H^+$$

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1) S. Jones and F. A. Long, *J. Phys. Chem.*, **56**, 25 (1952).
2) N. Tanaka, R. Tamamushi and M. Kodama, *Z. physik. Chem. (Frankfurt)*, **14**, 141 (1958).
3) N. Tanaka, K. Kato and R. Tamamushi, This Bulletin, **31**, 283 (1958).
4) C. M. Cook, Jr. and F. A. Long, *J. Am. Chem. Soc.*, **80**, 33 (1958).
5) N. Tanaka and K. Kato, unpublished.
6) W. Stricks and I. M. Kolthoff, *J. Am. Chem. Soc.*, **78**, 2085 (1956).
7) N. Tanaka, *J. Japan. Chem. (Kagaku no Ryoiki)*, **10**, 814 (1956).
8) N. Tanaka and T. Koizumi, This Bulletin, **30**, 303 (1957).
9) Y. Okinaka and I. M. Kolthoff, *J. Am. Chem. Soc.*, **79**, 3326 (1957).
10) I. M. Kolthoff and Y. Okinaka, *Anal. Chim. Acta*, **18**, 83 (1958).
11) N. Tanaka, T. Koizumi, T. Murayama, M. Kodama and Y. Sakuma, ibid., **18**, 97 (1958).
12) I. M. Kolthoff, Y. Okinaka and T. Fujinaga, ibid., **18**, 295 (1958).
13) N. Tanaka and K. Kato, This Bulletin, **32**, 516 (1959).

$$NiOAc^+ + H_2Y^{2-} \xrightarrow{k_{2b}} NiH_2Y + OAc^- \quad (7)$$
$$NiH_2Y \rightleftarrows NiHY^- + H^+ \rightleftarrows NiY^{2-} + 2H^+$$

From reactions 4 and 5, the rate of the decrease of $[Ni^{2+}]$ is expressed as,

$$-\frac{d[Ni^{2+}]}{dt} = k_{1a}[Ni^{2+}][HY^{3-}] + k_{2a}[Ni^{2+}][H_2Y^{2-}]$$
$$= \left\{k_{1a}\frac{K_{H_2Y}}{[H^+]} + k_{2a}\right\}[Ni^{2+}][H_2Y^{2-}] \quad (8)$$

where K_{H_2Y} represents the dissociation constant of H_2Y^{2-} ($=[HY^{3-}][H^+]/[H_2Y^{2-}]$). From reactions 6 and 7 the rate of the decrease of $[NiOAc^+]$ is expressed as,

$$-\frac{d[NiOAc^+]}{dt} = k_{1b}[NiOAc^+][HY^{3-}] + k_{2b}[NiOAc^+][H_2Y^{2-}]$$
$$= \left\{k_{1b}\frac{K_{H_2Y}}{[H^+]} + k_{2b}\right\}[NiOAc^+][H_2Y^{2-}] \quad (9)$$

The quantity of nickel(II) that is determined polarographically in acetate buffer is not the quantity of the hydrated nickel(II) ion, but the sum of those of the monoacetato- and the hydrated nickel ions[13]. If the sum is denoted by $[Ni^{2+}]_{app.}$,

$$[Ni^{2+}]_{app.} = [Ni^{2+}] + [NiOAc^+] \quad (10)$$

Therefore, the rate of the decrease of nickel(II) that is followed by the polarographic method is given as,

$$-\frac{d[Ni^{2+}]_{app.}}{dt} = -\frac{d\{[Ni^{2+}] + [NiOAc^+]\}}{dt}$$
$$= -\left\{\frac{d[Ni^{2+}]}{dt} + \frac{d[NiOAc^+]}{dt}\right\} \quad (11)$$

As for the EDTA present in the acetate buffer, the total concentratration of uncomplexed EDTA, $[EDTA]_f$, is represented by

$$[EDTA]_f = [HY^{3-}] + [H_2Y^{2-}] + [H_3Y^-] \quad (12)$$

From Eq. 12, $[H_2Y^{2-}]$ is given as

$$[H_2Y^{2-}] = \frac{[EDTA]_f}{\frac{[H^+]}{K_{H_3Y}} + 1 + \frac{K_{H_2Y}}{[H^+]}} \quad (13)$$

where K_{H_3Y} is the dissociation constant of H_3Y^- ($=[H_2Y^{2-}][H^+]/[H_3Y^-]$). The concentration of $NiOAc^+$ is written with the formation constant (K_{NiOAc}) and the concentrations of Ni^{2+} and OAc^-,

$$[NiOAc^+] = K_{NiOAc}[Ni^{2+}][OAc^-] \quad (14)$$

Introducing Eq. 14 into Eq. 10, $[Ni^{2+}]$ is given by

$$[Ni^{2+}] = \frac{[Ni^{2+}]_{app.}}{1 + K_{NiOAc}[OAc^-]} \quad (15)$$

Introducing Eqs. 8 and 9 into Eq. 11 and substituting Eq. 14 for $[NiOAc^+]$, we obtain

$$-\frac{d[Ni^{2+}]_{app.}}{dt} = \left[\left\{k_{1a}\frac{K_{H_2Y}}{[H^+]} + k_{2a}\right\} + \left\{k_{1b}\frac{K_{H_2Y}}{[H^+]} + k_{2b}\right\}K_{NiOAc}[OAc^-]\right][Ni^{2+}][H_2Y^{2-}] \quad (16)$$

Replacing $[H_2Y^{2-}]$ and $[Ni^{2+}]$ by the expressions given in Eqs. 13 and 15, respectively, and rearranging the resulted equation, Eq. 17 is obtained. Eq. 17 represents the overall rate expression for the complex-forming reaction between nickel(II) and EDTA whose reaction mechanisms are given by Eqs. 4 to 7. If $[H^+]$ and $[OAc^-]$ are not varied while the reaction proceeds, Eq. 17 can be written as

$$-\frac{d[Ni^{2+}]_{app.}}{dt} = k_{app.}[Ni^{2+}]_{app.}[EDTA]_f \quad (18)$$

where $k_{app.}$ means an apparent rate constant and corresponds to Eq. 19. The magnitude of $k_{app.}$ is dependent on both pH and the acetate concentration of the solution.

Experimental

Reagents.—A stock solution of disodium ethylenediaminetetraacetate was prepared by dissolving the commercial guaranteed reagent, and

$$-\frac{d[Ni^{2+}]_{app.}}{dt} = \frac{\{k_{1a} + k_{1b}K_{NiOAc}[OAc^-]\}\frac{K_{H_2Y}}{[H^+]} + \{k_{2a} + k_{2b}K_{NiOAc}[OAc^-]\}}{\{1 + K_{NiOAc}[OAc^-]\}\left\{\frac{[H^+]}{K_{H_3Y}} + 1 + \frac{K_{H_2Y}}{[H^+]}\right\}}[Ni^{2+}]_{app.}[EDTA]_f \quad (17)$$

$$k_{app.} = \frac{\{k_{1a} + k_{1b}K_{NiOAc}[OAc^-]\}\frac{K_{H_2Y}}{[H^+]} + \{k_{2a} + k_{2b}K_{NiOAc}[OAc^-]\}}{\{1 + K_{NiOAc}[OAc^-]\}\left\{\frac{[H^+]}{K_{H_3Y}} + 1 + \frac{K_{H_2Y}}{[H^+]}\right\}} \quad (19)$$

standardized against the standard copper(II) solution by amperometric titration using a dropping mercury electrode as an indicator electrode[14]. The copper(II) solution was prepared by dissolving recrystallized copper(II) sulfate, and its concentration was determined by electrogravimetry at constant potential by means of a Yanagimoto automatic potentiostat. The standard solution of nickel nitrate was obtained in the following way[15]. The alcoholic solution of dimethylglyoxime was added to the dilute solution of guaranteed nickel(II) nitrate. The precipitates were filtered and dissolved in guaranteed nitric acid. The nickel(II) solution obtained was made ammoniacal and subjected to the electrolysis. The nickel metal deposited was weighed accurately, dissolved in guaranteed nitric acid and diluted to the desired concentration with redistilled water. The concentration of nickel(II) of the solution was determined with the standard EDTA solution by amperometric trtration[16]. The concentration obtained was in good agreement with that determined by electrogravimetry.

Acetic acid-sodium acetate buffers were prepared with guaranteed sodium carbonate and acetic acid. Polyoxyethylene lauryl ether (LEO) with a mean molecular weight of 862 was used for a maximum suppressor. Other chemicals used were of guaranteed reagent grade.

Apparatus and Procedure.—The rate of the reaction between nickel(II) and EDTA was followed by measuring the change of the polarographic diffusion current of the nickel(II) with time. The current-time curves were recorded with a Yanagimoto Model PB-4 pen-recording polarograph using a rotated dropping mercury electrode (RDME)[6-12].

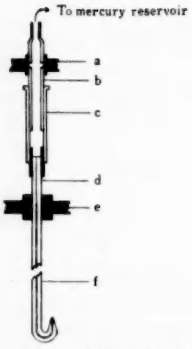

Fig. 1. Assembly of the RDME: a, fixed holder; b and c, inner and outer tubes of a 2 ml. syringe; d, capillary; e, holder of rotating apparatus; f, end tube.

14) N. Tanaka, M. Kodama, M. Sasaki and M. Sugino, *Japan Analyst* (*Bunseki Kagaku*), **6**, 86 (1957).
15) F. P. Treadwell and W. T. Hall, "Analytical Chemistry", Vol. 2, 9th ed., John Wiley and Sons, Inc., New York (1952), p. 193.
16) R. Přibil and B. Matyska, *Collection Czechoslov. Chem. Communs.*, **16**, 139 (1951).

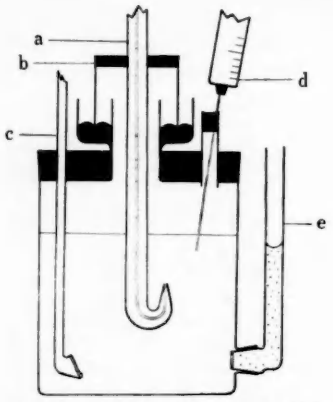

Fig. 2. Electrolysis cell: a, RDME; b, mercury seal; c, N_2 gas disperser; d, syringe; e, KNO_3-agar bridge.

In Fig. 1 is shown the RDME used in this study, which was similar to that reported by Okinaka and Kolthoft[9], being driven by means of a synchronous motor (Type A, provided with gears for speeds of 100, 150, 200 and 300 r.p.m., constructed by Yanagimoto Co., Ltd.). The electrode had an m value of 25.43 mg./sec. and a drop time of 2.95 sec. at 100 r.p.m., being measured at −0.60 volt vs. S.C.E. in air-free 0.2 M potassium nitrate solution containing 5×10^{-6} M LEO at 51.2 cm. of mercury head at 25°C.

The electrolysis cell in which the reaction took place was of a beaker-type of 100 ml. capacity as shown in Fig. 2. The cell was connected to a saturated calomel electrode through a potassium nitrate agar bridge. Special precautions were taken against the intrusion of atmospheric oxygen into the electrolysis cell during the measurement. A mercury seal was attached for this purpose. (See Fig. 2). The nitrogen gas was introduced into the solution through a gas disperser before and also during the measurement. The current measurement with the RDME was not disturbed by bubbling the gas through the solution. The rate of the flow of nitrogen gas was kept constant, being controlled by means of a flow-meter. The fluctuation of the residual current due to the change of the oxygen concentration was controlled within 0.05 microampere.

All kinetic measurements were made in acetate buffers of pH 3.8 to 5.2 at 0°C. The acetate concentrations were varied from 0.02 M to 0.1 M. The ionic strength was adjusted to be 0.2 with potassium nitrate. LEO was added as a maximum suppressor by 5×10^{-6} M in concentration. The pH of the solution was measured with a Hitachi Model EHP-1 pH meter, immediately after the measurements of current-time curves, within the accuracy of 0.02 pH unit.

The reaction was initiated by adding the air-free solution of the equivalent EDTA into the deaerated nickel(II) solution in the electrolysis

cell with the aid of a calibrated 1 ml. syringe. Since the RDME was driven and the nitrogen gas was bubbled throughout the measurement, reproducible current-time curves were able to be obtained immediately after the injection of the EDTA solution.

Results

A typical polarogram of nickel(II) which was obtained with 2×10^{-4} M Ni(II) in acetate buffer of pH 4.6 with the RDME is shown in Fig. 3. Although the limiting current plateau of the polarogram is not well-defined, the proportionality was found between the concentration of nickel(II) and the current that was measured at −1.35 V. vs. S.C.E. and corrected for the residual current, unless the concentration of nickel(II) exceeded 5×10^{-4} M. Therefore, current-time curves of the reaction mixtures were recorded at this potential. Typical examples of the current-time curves are reproduced in Fig. 4. Those curves were recorded at varied pH's with reaction mixtures in which the initial concentrations of nickel(II) and EDTA were each 1.00×10^{-4} M and the concentration of acetate was 0.1 M. It is expected from Eq. 18 that a plot of the reciprocal of $[Ni^{2+}]_{app.}$ against time gives a straight line with a slope of $k_{app.}$ Some of the plots are given in Fig. 5, from which the values of $k_{app.}$ were determined.

The current-time curves were obtained

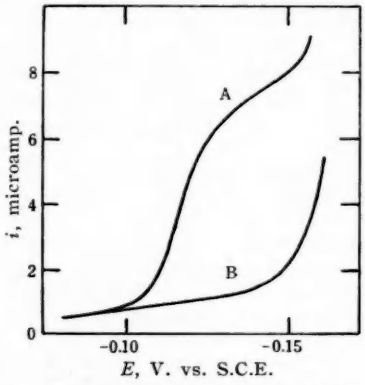

Fig. 3. Current-voltage curves of 2×10^{-4} M Ni(II) (curve A) and Ni(II)-EDTA (curve B) obtained at 0°C in acetate buffer-potassium nitrate solution of pH 4.6 and ionic strength 0.2 containing 0.1 M acetate and 5×10^{-6} M LEO.

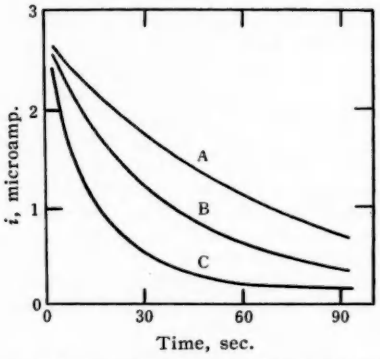

Fig. 4. Limiting current-time relation of the reaction between nickel(II) and EDTA, measured at −1.35 V. vs. S.C.E. at 0°C in acetate buffer-potassium nitrate solution of ionic strength 0.2 containing 0.1 M acetate and 5×10^{-6} M LEO, at pH 3.9 (curve A), pH 4.4 (curve B) and pH 5.0 (curve C). Initial concentrations of nickel(II) and EDTA are each 1.00×10^{-4} M.

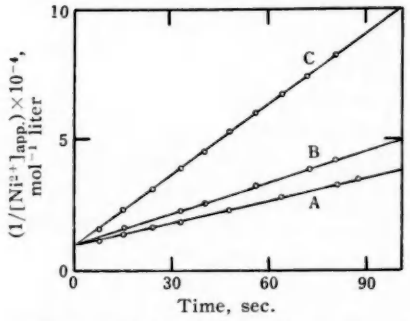

Fig. 5. Relation between the reciprocal nickel concentration and the time. Plots A, B and C are obtained from curves A, B and C in Fig. 4, respectively.

TABLE I. TYPICAL EXAMPLES OF THE RATE MEASUREMENT*

pH(0°C)	$[H^+]\times10^4$, mol./l.	$\frac{[H^+]}{K_{H_3Y}}$	$\frac{K_{H_2Y}}{[H^+]}$	$k_{app.}\times10^{-2}$, $(mol./l.)^{-1}$ sec^{-1}
4.03	1.197	0.06	0.00	3.02
4.09	1.044	0.05	0.00	3.18
4.14	0.928	0.04	0.01	3.26
4.55	0.361	0.02	0.01	4.54
4.72	0.244	0.01	0.02	5.43
4.94	0.148	0.01	0.03	6.70
5.01	0.125	0.01	0.04	7.60
5.16	0.089	0.00	0.06	10.0_0
5.21	0.079	0.00	0.07	10.3_3
5.26	0.071	0.00	0.08	11.2_5

* The solutions contain 0.05 M acetate. The initial concentrations of nickel(II) and EDTA are each 1.00×10^{-4} M.

at varied pH's in the range of pH 3.8 to 5.2 and at three different concentrations of acetate. It was found that the analysis of the current-time curves which were obtained with different initial concentrations of the reactants but at the same pH and acetate concentration gave the same $k_{app.}$. This fact confirmed that the reaction in question is of second order.

The magnitudes of $k_{app.}$ were determined at varied pH's and at three different concentrations of acetate. Examples of the experimental results which were obtained at 0.05 M acetate are given in Tabele I. From Eq. 19,

$$\begin{aligned}\alpha\beta k_{app.} &= \{k_{1a}+k_{1b}K_{\mathrm{NiOAc}}[\mathrm{OAc}^-]\}\frac{K_{\mathrm{H_2Y}}}{[\mathrm{H}^+]} \\ &\quad +\{k_{2a}+k_{2b}K_{\mathrm{NiOAc}}[\mathrm{OAc}^-]\} \\ &= k_1\frac{K_{\mathrm{H_2Y}}}{[\mathrm{H}^+]}+k_2 \qquad (20)\end{aligned}$$

$$\alpha=\frac{[\mathrm{H}^+]}{K_{\mathrm{H_3Y}}}+1+\frac{K_{\mathrm{H_2Y}}}{[\mathrm{H}^+]}$$

$$\beta=1+K_{\mathrm{NiOAc}}[\mathrm{OAc}^-]$$

$$k_1=k_{1a}+k_{1b}K_{\mathrm{NiOAc}}[\mathrm{OAc}^-]$$

$$k_2=k_{2a}+k_{2b}K_{\mathrm{NiOAc}}[\mathrm{OAc}^-]$$

are obtained. Eq. 20 indicates that a plot of the values of $\alpha\beta k_{app.}$ against the reciprocal of the hydrogen ion concentration should give a straight line, if $k_{app.}$'s were determined at the same concentration of acetate. The plots with the observed values of $k_{app.}$ gave the straight lines as shown in Fig. 6. The slope gave the value of $k_1K_{\mathrm{H_2Y}}$ in Eq. 20 and the intercept at $1/[\mathrm{H}^+]=0$, that of k_2. The relation between $\alpha\beta k_{app.}$ and the reciprocal of the hydrogen ion concentration was also treated by the method of least squares. The mean values and the probable errors of k_1 and k_2 were calculated as given in Table II.

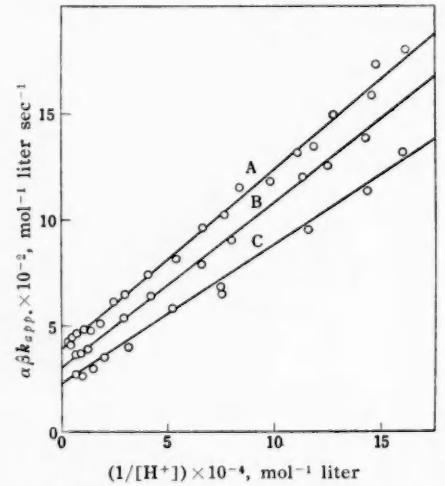

Fig. 6. Relations between $\alpha\beta k_{app.}$ and $1/[\mathrm{H}^+]$ obtained at 0°C in acetate buffer-potassium nitrate solution of ionic strength 0.2 at acetate concentrations 0.10 M (curve A), 0.05 M (curve B) and 0.02 M (curve C).

TABLE II. OBSERVED VALUES OF k_1 AND k_2

Concn. of acetate, M	$k_1\times10^{-4}$, mol^{-1} liter sec^{-1}	$k_2\times10^{-2}$, mol^{-1} liter sec^{-1}
0.10	$1.73\pm0.01_6$	$3.89\pm0.06_7$
0.05	$1.41\pm0.01_9$	$2.95\pm0.15_3$
0.02	$1.18\pm0.00_9$	$2.42\pm0.07_6$

The hydrogen ion concentration used in this calculation was derived from the pH observed and the activity coefficient of the hydrogen ion. The pH of the solution was measured at 25°C and corrected for temperature to be reduced to the value at 0°C. The activity coefficient of the hydrogen ion was calculated to be 0.78 at 0°C and ionic strength 0.2 according to Kielland[17]. The third dissociation constant of EDTA, $K_{\mathrm{H_3Y}}$, which was determined by Schwarzenbach and Ackermann[18] at 20°C and $\mu=0.1$, was used after correction for ionic strength and temperature. The ion size parameters of H_2Y^{2-} and HY^{3-} were assumed to be the same as that of suberic acid given by Kielland[17]. The temperature correction for $K_{\mathrm{H_2Y}}$ was made with the aid of the ΔH value reported by Carini and Martell[19]. The resulted value of $K_{\mathrm{H_2Y}}$ was $10^{-6.27}$. On the other hand, there has been no publication concerning the temperature coefficient of $K_{\mathrm{H_3Y}}$. In this calculation, therefore, the value of $10^{-2.67}$, which was obtained by Schwarzenbach and Ackermann[18] at 20°C and $\mu=0.1$, was used without further correction. Since this constant is concerned only with the calculation of α, in which the contribution of the term $[\mathrm{H}^+]/K_{\mathrm{H_3Y}}$ does not exceed 10% under the present condition, the use of $K_{\mathrm{H_3Y}}$ without correction seems to introduce no significant error into the calculation of the rate constant.

17) J. Kielland, *J. Am. Chem. Soc.*, **59**, 1675 (1937).
18) G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **30**, 1798 (1947).
19) F. F. Carini and A. E. Martell, *J. Am. Chem. Soc.*, **75**, 4810 (1953).

The formation constant of the monoacetatonickel(II) complex, K_{NiOAc}, was determined to be 3.0 at 0°C, by extrapolating the values obtained at 15°, 25° and 35°C in the solution of ionic strength 0.2[13].

From k_1 and k_2 in Table II, the values of k_{1a}, k_{1b}, k_{2a} and k_{2b} were calculated as given in Table III.

TABLE III. RATE CONSTANTS OF VARIOUS NICKEL(II)-EDTA REACTIONS

Reaction	Rate constant, mol^{-1} liter sec^{-1}
$Ni^{2+}+HY^{3-} \xrightarrow{k_{1a}} NiHY^-$	$1.0_6\times10^4$
$NiOAc^+ + HY^{3-} \xrightarrow{k_{1b}} NiHY^- + OAc^-$	$2.2_5\times10^4$
$Ni^{2+}+H_2Y^{2-} \xrightarrow{k_{2a}} NiH_2Y$	$2.0_4\times10^2$
$NiOAc^+ + H_2Y^{2-} \xrightarrow{k_{2b}} NiH_2Y + OAc^-$	$6.0_4\times10^2$

Discussion

The complex-forming reaction of nickel with ethylenediaminetetraacetate was found to proceed through four different reaction paths given in Eqs. 4 to 7 in acetate buffers of pH 3.8 to 5.2. The rate constants of those four elementary reactions were determined. It seems reasonable that the reactions involving HY^{3-} species are much faster than those involving H_2Y^{2-}.

On the other hand, the effect of acetate ions on the reaction rate was rather unexpected. The previous studies on the displacement reactions involving metal-EDTA complexes indicated that the reaction rate decreased with increasing concentration of acetate[20,21]. The rate of the complex-forming reaction between nickel (II) and EDTA, however, was found to decrease with decreasing concentration of acetate. The rate constants of the reactions involving the monoacetatonickel(II) ions were nearly twice as great as those of the corresponding reactions involving the hydrated nickel ions. A similar phenomenon was reported by Wilkins[22], who studied the exchange reaction involving the nickel(II)-2,3-diamino-2,3-dimethylbutane complex and observed the faster reaction rate in the presence of ammonium acetate. Although the effect of acetate on the nickel-EDTA reaction is not completely solved at the present moment, it may not be unreasonable to consider the decrease of the activation energy of the reaction as being due to the acetate co-ordinated.

It seems interesting to compare the rate constants obtained in this study with those obtained by Cook and Long[4]. They studied the exchange reaction between nickel(II) and nickel(II)-EDTA complexes with the aid of the radioactive isotope at 25°C and ionic strength 0.1, and determined the rate constants of several reaction paths including the following:

$$NiY^{2-} + H^+ \rightleftarrows Ni^{2+} + HY^{3-} \quad (21)$$

$$NiHY^- + H^+ \rightleftarrows Ni^{2+} + H_2Y^{2-} \quad (22)$$

The reactions given by Eqs. 21 and 22 correspond to the reverse of those given by Eqs. 4 and 5, respectively. The equilibrium constants of reactions 21 and 22,

$$K(\text{Eq. 21}) = [Ni^{2+}][HY^{3-}]/[NiY^{2-}][H^+] = 1/K_{NiY}K_{HY}$$

$$K(\text{Eq. 22}) = [Ni^{2+}][H_2Y^{2-}]/[NiHY^-][H^+] = 1/K_{NiY}K^{H}_{NiHY}K_{HY}K_{H_2Y}$$

were calculated, where K_{NiY} represents the formation constant of NiY^{2-}, K_{HY} and K_{H_2Y} the dissociation constants of HY^{3-} and H_2Y^{2-}, respectively, and K^{H}_{NiHY} the equilibrium constant of the reaction,

$$NiY^{2-} + H^+ \rightleftarrows NiHY^-$$

The values of K_{HY}, K_{H_2Y}, K_{NiY} and K^{H}_{NiHY} which were determined by Schwarzenbach and his co-workers[18,23] at 20°C and $\mu = 0.1$ were used without further correction. With the equilibrium constants obtained and the rate constants given by Cook and Long, the rate constants for the reverse reactions of Eqs. 21 and 22 were calculated and compared with k_{1a} and k_{2a} as shown in Table IV.

Unfortunately, Cook and Long did not take into account the effect of the acetate

TABLE IV. COMPARISON OF THE RATE CONSTANTS

Reaction	Rate constant, mol^{-1} liter sec^{-1}: Calculated from data at 25°C given by Cook and Long[4]	Observed at 0°C in this study
$Ni^{2+}+HY^{3-} \longrightarrow NiHY^-$	3.0×10^5	$1.0_6\times10^4$
$Ni^{2+}+H_2Y^{2-} \longrightarrow NiH_2Y$	8.1×10^2	$2.0_4\times10^2$

20) H. Ackermann and G. Schwarzenbach, *Helv. Chim. Acta*, **35**, 485 (1952).
21) N. Tanaka and K. Kato, unpublished.
22) R. G. Wilkins, *J. Chem. Soc.*, **1957**, 4521.
23) G. Schwarzenbach, R. Gut and G. Anderegg, *Helv. Chim. Acta*, **37**, 937 (1954).

on the reaction mechanisms and gave no information of the concentration of acetate present in their reaction mixtures. Therefore, the rate constants given by those authors do not exactly correspond to those given in this study. Nevertheless, it may be concluded that the results obtained in both investigations are in reasonable agreement.

Bjerrum and Poulsen[24] studied the kinetics of the formation of nickel(II) and copper(II) complexes of ethylenediamine in methanol at 0°C. They found that copper(II) complexes are more labile than the corresonding nickel(II) compounds. The rate constants of the formation of $Ni(en)^{2+}$ was 2.5×10^{4} mol^{-1} liter sec^{-1} and that of $Cu(en)^{2+}$, 5×10^{11} mol^{-1} liter sec^{-1}, where en denotes ethylenediamine.

Recent studies[3,5] in this laboratory revealed that the rate constants of the formation of copper(II) and lead(II) complexes of EDTA through the reaction

$$M^{2+}+HY^{3-} \rightleftarrows MY^{2-}+H^{+}$$
(M=Cu or Pb)

range from 10^{9} to 10^{11} mol^{-1} liter sec^{-1} at room temperature. The slower rate of the formation of nickel(II)-EDTA complexes is apparent as in the case of the formation of nickel-ethylenediamine complexes.

Summary

The complex-forming reaction of nickel (II) with ethylenediaminetetraacetate (EDTA) was found to proceed in acetate buffers of pH 3.8 to 5.2 through four different reaction paths,

$$Ni^{2+}+HY^{3-} \xrightarrow{k_{1a}} NiHY^{-}$$

$$NiOAc^{+}+HY^{3-} \xrightarrow{k_{1b}} NiHY^{-}+OAc^{-}$$

$$NiHY^{-} \rightleftarrows NiY^{2-}+H^{+}$$

$$Ni^{2+}+H_2Y^{2-} \xrightarrow{k_{2a}} NiH_2Y$$

$$NiOAc^{+}+H_2Y^{2-} \xrightarrow{k_{2b}} NiH_2Y+OAc^{-}$$

$$NiH_2Y \rightleftarrows NiHY^{-}+H^{+} \rightleftarrows NiY^{2-}+2H^{+}$$

The change in the polarographic diffusion current of nickel(II) at the rotated dropping mercury electrode was utilized to follow the decrease of the nickel(II) concentration in the reaction mixture after the initiation of the reaction. The rate constants of the reaction paths were determined at 0°C and ionic strength 0.2, with the results:

$k_{1a}=1.0_6\times10^{4}$ mol^{-1} liter sec^{-1}
$k_{1b}=2.2_5\times10^{4}$ 〃
$k_{2a}=2.0_4\times10^{2}$ 〃
$k_{2b}=6.0_4\times10^{2}$ 〃

These constants are much smaller than those of the corresponding reactions between copper(II) and EDTA.

The authors thank the Ministry of Education for the financial support granted for this research.

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24) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", John Wiley & Sons, Inc., New York (1958), p. 204.

*Cation Arrangement in Lithium Ferrospinel-Lithium Aluminospinel Solid Solution**

By Eizo KATO**

(Received September 25, 1958)

A cation arrangement in a spinel structure shows how some cations of different valencies are distributed at tetrahedral interstices of the 8-fold position or octahedral ones of the 16-fold position in a spinel lattice, and it has given very interesting subjects concerning a correlation between crystal structure and physico-chemical properties. From the crystallographic aspect a spinel structure is specified into a normal and an inverse type by some difference of the cation arrangement, and only the ferrospinel of inverse structure can reveal ferromagnetism. These fruitful works in solid state physics were presented by Verwey and his co-workers' experiments[1] and by Néel's theory[2].

Cation arrangement in 2—3 ferrospinel*** solid solution, e.g., nickel-zinc ferrospinel, has been studied not only from the scientific aspect but also in reference to the improvement of magnetic materials[3]. At present the arrangement of trivalent cations is aimed at which is studied in nickel ferro-aluminospinel[4] and other ferro-aluminospinel solid solutions[1]. In the previous paper[5] LFS-LAS solid solution was found to show an order-disorder transition, in addition to showing properties seen in other ferro-aluminospinel solid solutions. On purpose to know correlations between the cation arrangements and other physico-chemical properties, X-ray diffraction intensities were measured and simple magnetic measurements were also carried out.

Experimental

Specimens.—Specimens were synthesized and heat-treated by the method mentioned already[5]. Specimen codes were A (=LAS), B, C, P, R, Q, D, E and F (=LFS), according to each chemical composition as is shown in Table I. The subscript "L" or "H" was supplied behind the code name of a specimen to show whether it was of ordered or disordered phase.

Apparatus.—X-ray diffraction intensities were measured by Norelco X-ray diffractometer with Co K_α radiation.

Magnitude of magnetization was determined by means of the measurement of distances at which small rods of a sample with dimensions (ca. 0.2 mm. diameter, ca. 3 mm. length) can be attracted by a magnet so as to give a definite attractive force.

Results and Discussion

A general expression of the cation arrangement in LFS-LAS solid solution, $LiFe_pAl_{(5-p)}O_8$, is as follows:

$$[Li_xFe_yAl_{(2-x-y)}]_{tet}\,[Li_{(1-x)}Fe_{(p-y)}Al_{(3+x+y-p)}]_{oct}O_8$$

where subscript "tet" means the tetrahedral site and "oct" the octahedral site. x and y are the numbers of lithium ions and ferric ions, respectively, located in the tetrahedral site. Then, the average atomic scattering factor for the cation mixture existing in the tetrahedral or the octahedral site, i.e., $\langle f_{tet}\rangle$ or $\langle f_{oct}\rangle$, is written as

$$2\langle f_{tet}\rangle = xf_{Li} + yf_{Fe} + (2-x-y)f_{Al}$$

$$4\langle f_{oct}\rangle = (1-x)f_{Li} + (5-y)f_{Fe} + (3+x+y-p)f_{Al}$$

where f_{Li} is the atomic scattering factor of lithium ion, f_{Fe} of ferric ion and f_{Al} of aluminum ion.

A cation arrangement in LFS is shown as $[Li_xFe_{(2-x)}]_{tet}[Li_{(1-x)}Fe_{(3+x)}]_{oct}O_8$, and $\langle f_{tet}\rangle$ and $\langle f_{oct}\rangle$ are written as

---

* Lithium ferrospinel and lithium aluminospinel are abbreviated to LFS and LAS, respectively, in the following.

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1) For instances, E. J. W. Verwey and E. L. Heilmann, *J. Chem. Phys.*, **15**, 174 (1947); E. J. W. Verwey, P. W. Haayman and F. C. Romeijn, ibid., **15**, 181 (1947); E. J. W. Verwey, P. B. Braun, E. W. Gorter, F. C. Romeijn and J. H. van Santen, *Z. physik. Chem.*, **198**, 6 (1951).

2) L. Néel, *Ann. phys.*, [12], **3**, 137 (1948).

*** 2—3 spinel means the spinel with di- and tri-valent cations.

3) For instance, R. L. Harvey, I. J. Hegyi and H. W. Leverenz, *RCA Rev.*, **11**, 321 (1950).

4) E. W. Gorter, *Nature*, **173**, 123 (1954); J. S. Smart, *Phys. Rev.*, **94**, 847 (1954).

5) E. Kato, This Bulletin, **32**, 51 (1959).

$$2\langle f_{tet}\rangle = xf_{Li} + (2-x)f_{Fe}$$

$$4\langle f_{oct}\rangle = (1-x)f_{Li} + (3+x)f_{Fe}$$

The same procedure is available in case of LAS. Values of the structure amplitude for reflections were calculated through the above expressions.

Integrated intensity P, which is estimated from structure amplitude F, is proportional to diffractometric peak area A, i. e.,

$$\frac{A_{hkl}}{A_{lmn}} = \frac{P_{hkl}}{P_{lmn}} = \frac{[mF^2(1+\cos^2 2\theta)\operatorname{cosec}^2\theta\sec\theta]_{hkl}}{[mF^2(1+\cos^2 2\theta)\operatorname{cosec}^2\theta\sec\theta]_{lmn}}$$

where $h\,k\,l$ and $l\,m\,n$ show Miller's indices for two arbitrary reflections, m=multiplicity and θ=Bragg angle. By measurements of X-ray diffraction intensities for the fundamental reflections, which appear regardless of the existence of a superstructure in the crystal lattice, the cation arrangements can be determined not only in the disordered phase but also in the ordered phase by the above procedures. In order to estimate the cation arrangements in LFS, LAS and LFS-LAS solid solution, reflections 220, 311 and 400 were chosen. The values of the peak area are listed in Table I.

The cation arrangements in LFS and LAS**** are listed in Table II. In this table $[Fe_{2.0}]_{tet}[Li_{1.0}Fe_{3.0}]_{oct}O_8$ was given at both the ordered phase (FL) and the disordered phase (FH) of LFS, which agree with Braun's report[6]. At the ordered phase of LAS, AL, the cation arrangement is expressed in $[Li_{0.3}Al_{1.7}]_{tet}[Li_{0.7}Al_{3.3}]_{oct}O_8$ which also agrees with $[Li_{1/3}Al_{5/3}]_{tet}[Li_{2/3}Al_{10/3}]_{oct}O_8$ given by Verwey[3]. The error in x measurement decreases with increase in peak area, and the accuracy of x was estimated to range within ± 0.05 for LFS and within ± 0.1 for LAS.

To determine the cation arrangement in LFS-LAS solid solutions[7], it is necessary to assume an adequate value for x, because x and y are variables dependent on each other for any kind of reflection. The following postulations are offered;

1) In LAS a partition of lithium ions to the tetrahedral and to the octahedral site is proportional to that of aluminum ions. In LFS, lithium ions are located only in the octahedral site. In any LFS-LAS solid solution, it is assumed that the partitions of lithium and aluminum ions have the same value regardless of distribution of ferric ions, i. e.,

$$x/(1-x) = (2-x-y)/(3+x+y-p)$$

2) A structural parameter u for oxygen ion has near values both for LFS and for LAS, and u value is almost free in the calculations of structural amplitude in this case. Therefore, u in the solid solutions is assumed to have additive property.

The values of x and y are shown in Table I, and the resultant cation arrangements are listed in Table II. Though numerous errors may be found in the determination of x and y, qualitative conclusions can be proved from experiments of a series of specimens. Lithium ions and ferric ions are located in the different site in the ordered lattice of LFS. In LAS and LFS-LAS solid solution, lithium ions are insufficient in number to be arranged in their proper lattice points (the lithium sites), wherein lithium ions enter for the ordered state of LFS. It is expected that the lithium sites in LAS and LFS-LAS solid solution are occupied by all of the lithium ions in question and the remnants by a few aluminum ions or ferric ions divided into the octahedral site, because the diffraction intensities of LAS and of LFS-LAS solid solution have the same result as that of LFS. Therefore, the crystal structures of low-temperature forms of LAS and of LFS-LAS solid solutions may be considered as those of a sort of disordered state. The lattice points, where aluminum ions are exchanged for ferric ions, are mainly

AL→BL and QL→DL→EL at the tetrahedral site,

BL→CH→PH→RH→QL and EL→FL at the octahedral site.

In the previous paper[5], I have reported the distinction in physical properties between LFS-LAS solid solutions of iron-rich composition (above 68 mol. % LFS) and those of an aluminum-rich one (below 20 mol. % LFS). No change takes place in the cation arrangement at the octahedral site in spite of the change from AL to BL. It is considered that this fact makes the aluminum-rich solid solution stable in ordered state. The manner is similar for the cation exchange in the tetrahedral site from EL to FL. It is

**** As for structural parameter, u, following values were used; LFS: $u=0.382$[6]; LAS: $u=0.385$[1].

6) P. B. Braun, *Nature*, **170**, 1123 (1952).

7) For evaluating x and y, conditions to be satisfied are,

(i) $5\geqq p\geqq 0$ (ii) $p+1\geqq x+y\geqq p-3$, $2\geqq x+y\geqq 0$

(iii) $1\geqq x\geqq 0$ (iv) $p\geqq y\geqq p-4$, $2\geqq y\geqq 0$

TABLE I. DIFFRACTOMETRIC PEAK AREAS AND THE VALUES FOR x AND y

Specimen code	Composition, p	Peak area			x	y
		A_{220}	A_{311}	A_{400}		
AL	0	308	831	516	0.2_3	—
BL	1	696	1232	357	0.2_2	0.8_8
CH	1.5	723	1471	473	0.2_7	0.7_8
PH	2	710	1565	485	0.2_8	0.8_8
RH	2.5	865	1791	481	0.2_5	1.0_8
QL	3	815	1673	485	0.3_0	1.1_0
DL	3.5	724	1570	350	0.2_2	1.4_8
DH	3.5	642	1518	450	0.3_3	1.1_5
EL	4	956	2358	434	0.0_8	1.8_2
FL*	5	798	2036	—	-0.0_2	—
FH*	5	767	1902	—	-0.0_6	—

* Peak areas are given from the previous paper[5].

TABLE II. CATION ARRANGEMENT IN LFS-LAS SOLID SOLUTION

Specimen code	Tetrahed. lattice point	Octahed. lattice point
AL	$Li_{0.3}$ $Al_{1.7}$	$Li_{0.7}$ $Al_{3.3}$
BL	$Li_{0.2}$ $Fe_{0.9}$ $Al_{0.9}$	$Li_{0.8}$ $Fe_{0.1}$ $Al_{3.1}$
CH	$Li_{0.3}$ $Fe_{0.8}$ $Al_{0.9}$	$Li_{0.7}$ $Fe_{0.7}$ $Al_{2.6}$
PH	$Li_{0.3}$ $Fe_{0.9}$ $Al_{0.8}$	$Li_{0.7}$ $Fe_{1.1}$ $Al_{2.2}$
RH	$Li_{0.2}$ $Fe_{1.1}$ $Al_{0.7}$	$Li_{0.8}$ $Fe_{1.4}$ $Al_{1.8}$
QL	$Li_{0.3}$ $Fe_{1.1}$ $Al_{0.6}$	$Li_{0.7}$ $Fe_{1.9}$ $Al_{1.4}$
DL	$Li_{0.2}$ $Fe_{1.5}$ $Al_{0.3}$	$Li_{0.8}$ $Fe_{2.0}$ $Al_{1.2}$
DH	$Li_{0.3}$ $Fe_{1.2}$ $Al_{0.5}$	$Li_{0.7}$ $Fe_{2.3}$ $Al_{1.0}$
EL	$Li_{0.1}$ $Fe_{1.8}$ $Al_{0.1}$	$Li_{0.9}$ $Fe_{2.2}$ $Al_{0.9}$
FL, FH	$Fe_{2.0}$	$Li_{1.0}$ $Fe_{3.0}$

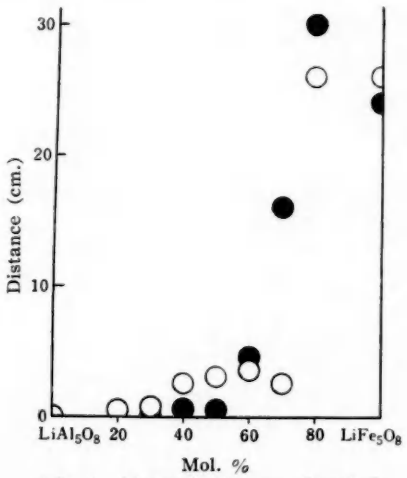

Fig. 1. Magnetization vs. chemical composition.
○: ordered phase
●: disordered phase

difficult at present to resolve physical changes in view of the cation arrangement.

Magnetism in a ferrospinel is explained by the theory of ferrimagnetism. Only ferric ions contribute to spontaneous magnetization in LFS-LAS solid solution, and the magnitude of magnetization is related both with the difference between numbers of ferric ions at the tetrahedral and at the octahedral site and with an interaction between cations at the tetrahedral and octahedral site (the latter relating to numbers of ferric ions located in two kinds of lattice point). Fig. 1 shows the relative magnitude of magnetization of LFS-LAS solid solutions at room temperature, measured by the distances capable of attracting specimens by a magnet, as a function of the chemical composition. The observed magnitudes of magnetization qualitatively agree with magnitudes presumed from the cation arrangement.

Now, a quenching effect of LFS-LAS solid solution will be discussed. In specimens C, P and R, magnitudes of magnetization in disordered phase were smaller than those in ordered phase. C, P and R in ordered phase were mixtures of two phases which roughly corresponded to B and D, so that magnetization of specimens was suitable to the resultant magnetization of two phases. When the configurational free energy of crystal lattice is scarcely changed by any cation arrangement, cations, owing to thermal agitation at high temperature, incline to be statistically distributed[8] rather than to be located in the most stable state. In CH, PH, RH, high-temperature form of E and FH, their statistical structures are not recognized. On the other hand, in D, the cation

8) "Statistical distribution" means that cations are distributed over all cation sites at random, while "disordered" phase as for ferrospinel indicates a phase in statistical distribution over the octahedral site alone.

arrangement in disordered phase differs from that in ordered phase, and its statistical distribution at a high temperature is recognized from magnetic measurements as well as from X-ray studies. In Q also, the magnetization in ordered phase results in the near magnitude to that in a disordered one, and the statistical distribution is demonstrated. Briefly summarizing, LFS-LAS solid solution gave different cation arrangements within the ordered and the disordered phase in general, but the possibility of the statistical distribution, as is shown in magnesium and cupric ferrospinels, can not yet be determined.

The author is indebted to Mr. Kazuo Sasaki of Osaka City University for his assistance in X-ray measurements.

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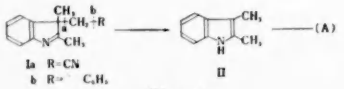
The Mechanism of Reductive Cleavage Reaction of 2,3-Dimethyl-3-cyanomethylindolenine

By Masao NAKAZAKI

(Received December 1, 1958)

Hoshino and Tamura[1] observed the unexpected formation of 2,3-dimethylindole(II) by the reduction of 2,3-dimethyl-3-cyanomethylindolenine(Ia) with sodium and ethanol.



Ia R=CN
b R= C_6H_5

Fig. 1

Recently, we have reported[2] a conversion of 3-alkyl-2,3-dimethylindolenines into 2,3-dimethylindole by means of acid, and proposed a mechanism which could not be applied to the explanation of the mechanism of Hoshino's reaction mentioned above.

In some cases, the reductive cleavage of $-CH_2CN$ to CH_3 was reported[3]; however, a search of the literature failed to find analogous reaction[4] to Hoshino's reductive cleavage by the action of sodium and ethanol.

The study of elucidation of the mechanism of this novel reductive cleavage reaction was undertaken with the hope that this might lead to some bits of information which would be able to be applied to the structure determination of the indole alkaloids.

The simplest, but not so attractive, explanation would be the hydrogenolysis of bond a (Fig. 1). Since in many instances, a benzyl group is noticed to be split off very easily under various reductive conditions, 2,3-dimethyl-3-benzylindolenine(Ib) was treated with sodium and ethanol as a model experiment. But, as would be expected, 2,3-dimethyl-3-benzylindoline, instead of II, was obtained from the reaction mixture, simply as the result of the reduction of indolenine double bond.

To examine another possible route, which would be initiated by an attack of ethoxide anion (Fig. 2. mechanism B), Ia was treated with sodium ethoxide in ethanolic solution.

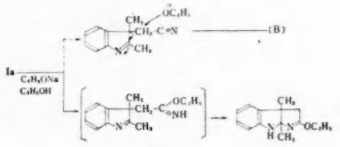


Fig. 2

It was unsuccessful to detect any trace of II, but a crystalline compound, m. p. 148~

1) T. Hoshino and K. Tamura, *Ann.*, **500**, 46 (1933).
2) M. Nakazaki, S. Isoe and K. Tanno, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **76**, 1262 (1955).
3) J. J. Bloch, *Chem. Zentr.*, III, 609 (1919); see also R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry", John Wiley and Sons, Inc., New York (1953), p. 659.
4) In the case of indole compounds, the vulnerability of bond b (Fig. 1) is noticed, e. g., F. C. Uhle and L. S. Harris, *J. Am. Chem. Soc.*, **79**, 103 (1957); H. R. Snyder and D. S. Mattson, ibid., **79**, 2217 (1957); E. Lecte and L. Marion, *Can. J. Chem.*, **31**, 775 (1953).

149°C, was isolated, the molecular formula of which corresponded to Ia plus one molecule of ethanol. This compound could be prepared also by the action of ethanolic hydrochloric acid onto Ia, and was given the structure IV by the observation of I. R. (see, experimental part) and U. V. spectrum (Fig. 7).

The failure of the conversion of Ia into II only by means of sodium ethoxide indicated that course B must be ruled out, and the reductive condition seems to be imperative for the change Ia→II.

The fact that it was found possible for the compound IV, in turn, to afford II by the action of potasium and *tert*-butanol, led to the conclusion that Ia is not the only compound capable of undergoing Hoshino's reaction. This was confirmed further by the isolation of II, when sodium was added to the ethanolic solution of the indolenine ester V, prepared from Ia by the alcoholysis with ethanol and concentrated sulfuric acid.

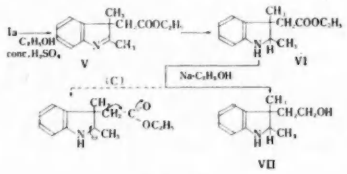


Fig. 3

The complexity encountered in the case of Ia suggested that the compound V appeared to be more suitable than Ia for the further study of Hoshino's reaction[5]. Having two reducible groups in the molecule, at the initial stage of the reaction, the compound V would be attacked by a reduction reagent either on the indolenine nucleus or on the side chain.

If the former is the case, the intermediate compound will be the compound VI which would give II, according to the mechanism C shown on Fig. 3. But VI, prepared by catalytic hydrogenation[6] of V with platinum oxide in acetic acid failed to afford II with sodium ethoxide or potassium *tert*-butoxide[7]. The reduction of VI with sodium and ethanol did not afford II either, but an alcohol VII was the sole product isolable from the reaction mixture. This alcohol was proved to be identical with the one prepared from VI by the lithium aluminum hydride reduction.

Thus, mechanism C had to be abandoned, and another conceivable route in which the reduction reagent would attack the side chain first was to be sought. To examine this possibility, an attempt was made to prepare the possible intermediate IX.

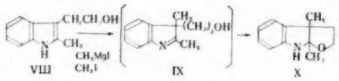


Fig. 4

The reaction of the Grignard complex of VIII with methyl iodide afforded a crystalline product, m. p. 51.5~52.5°C, to which the structure X[8] was assigned because of the lack of OH band but the presence of NH band in its I. R. spectrum, coupled with its indoline type absorption in the U. V. region (Fig. 7). This material again failed to give II, under the Hoshino's condition.

These observations lead one to conclude that: 1. the compounds of the general structure XI[9] (Fig. 5, where X is electronegative atom, such as oxygen or nitrogen.), furnish 2,3-dimethylindole with sodium and alcohol; 2. reduction reagent attacks simultaneously[10] the unsaturated bond of indolenine nucleus and the one on the side chain.

The most plausible mechanism, D, is shown on Fig. 5. A 1,4-biradical XII,

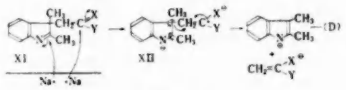


Fig. 5

5) Upon catalytic hydrogenation, V gave the compound VI as the result of the hydrogenation of the indolenine double bond, but in the case of Ia the side chain also would be reduced at the same time.

6) H. L. Holmes, H. T. Openshaw and R. Robinson, *J. Chem. Soc.*, **1946**, 910.

7) The formation of a small amount of *tert*-butyl ester by *tert*-butanolysis was presumed by effervescence of the crude picrate of recovered ester observed at its melting point.

8) T. Hoshino and K. Shimodaira (*Ann.*, **520**, 19 (1935)) succeeded in preparing the first compound which has the same skeleton as X, but they could decide whether their compound has the skeleton IX or X. Since our compound was established to have the structure X (3a, 8a-dihydro-3a,8a-dimethyl-2-furo [2.3-b] indole), their compound is 3a, 8a-dihydro-3a-methyl-2-furo [2.3-b] indole. See the nomenclature in "The Ring Index", by A. M. Patterson and L. T. Capell, Reinhold Pub. Corp., (1940), p. 198.

9) Under the reaction condition, the compound IV would be safely assumed to be converted back to III, which would be cleaved to give II. This causes a shift of equilibrum, and eventually all of IV would be transformed to II.

10) Though not necessarily at the very same instance, the reduction of one of two functional groups should not exceed the other, otherwise it would give either VI or X which can not give II.

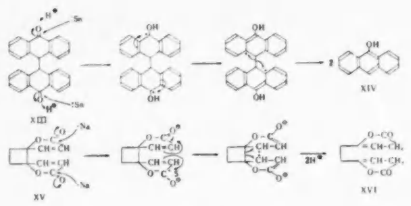


Fig. 6

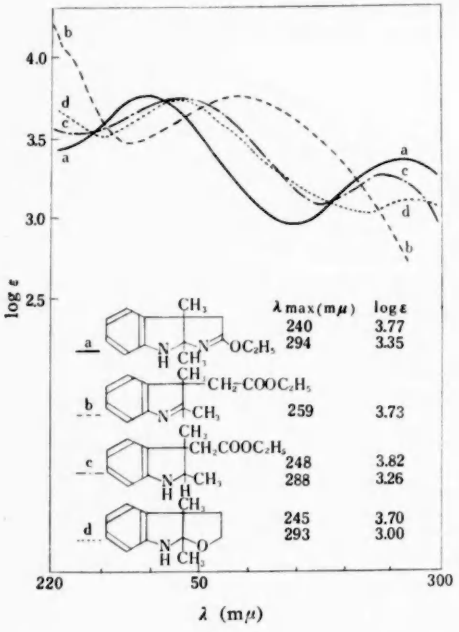


Fig. 7

which is caused by a nucleophilic attack[11] of the electron from sodium, is unstable[12] and suffered cleavage of bond a by the electron migration as indicated with arrows, resulting in end products.

According to this mechanism, in the case of Ia, the side chain split off is probably acetonitrile, which would be reduced further to give ethylamine. The actual isolation of ethylamine as the form of ethyloxamide from the reaction mixture of Hoshino's reaction of Ia, will support this mechanism.

The reductive cleavage of dihydrodianthrone(XIII) to anthrone(XIV)[13] with tin and acetic acid containing hydrochloric acid, and the conversion of anemonine (XV) into dihydroanemonine(XVI)[14] with sodium amalgam and acetic acid in methanolic solution appear to follow the analogous reaction pattern. (Fig. 6).

The driving force of the reaction could be sought in the steric strain of cyclobutane ring in the case of XV, and the tendency to aromatize into stable indole structure would play an important rôle in promoting Hoshino's reaction.

Experimental[15]

2,3-Dimethyl-3-cyanomethylindolenine(Ia). —Ia was prepared following Hoshino and Tamura's procedure[1]. Attempts were made to improve the yield by using methyl bromide in place of the ethyl iodide used in their synthesis or employing "reversed Grignard synthesis". The best result was obtained when chloroacetonitrile was added rather rapidly. Grignard solution prepared from 1.2 g. of magnesium and 8.0 g. of methyl iodide in 30 cc. of absolute ether was cooled and 7.3 g. of 2,3-dimethylindole in 35 cc. of ether was added dropwise onto it.

After the generation of methane subsided, the reaction mixture was stirred for 10 min. at room temperature and refluxed on a water bath for another 30 min. When 4.0 g. of chloroacetonitrile[16] was added during 5 min. into the cooled solution, a yellow viscous precipitate was observed on the wall of the reaction vessel.

After the solution was allowed to stand for 20 min. at room temperature, it was refluxed for 30 min. The Grignard complex was decomposed by the addition of 6 g. of acetic acid and 200 cc. of ice water, and the reaction mixture was thoroughly extracted with ether. Basic material was extracted by shaking with 2 N hydrochloric acid solution from the combined ether extract, and was precipitated from the solution as yellow oil by the addition of excess of 4 N sodium hydroxide solution. The oil was extracted with ether, and the ether extract was washed with water and dried over magnesium sulfate. Evaporation of

11) As for the action of sodium on organic compounds, see an excellent article by A. J. Birch, *Quart. Rev.*, **4**, 69 (1950).

12) R. C. Fuson, "Advanced Organic Chemistry", John Wiley and Sons, New York (1953), p. 72.

13) E. de Barry Barnett and M. A. Mathews, *J. Chem. Soc.*, **123**, 380 (1923).

14) Y. Asahina and R. Fujita, *J. Pharm. Soc. Japan* (*Yakugaku Zasshi*), **448**, 471 (1919); ibid., **455**, 1 (1920). The position of the double bonds of dihydroanemonine (XVI) deduced by this mechanism agrees with the one established by their experimental results.

15) All melting points are uncorrected. All U. V. spectra were measured with an EPS-2 Hitachi Autorecording Spectrophotometer and I. R. spectra on a Perkin Elmer Model 12C. The analyses were performed in the microanalytical laboratory of the Institute of Polytechnics, Osaka City University.

16) Since trimethylbenzene recommended as solvent is not easily accessible, the procedure described in "Organic Syntheses" (Vol. **30**, 22 (1950)) was simplified as follows. An intimate mixture of finely powdered chloroacetamide (1 mol.) and phosphorus pentoxide (2.5 mol.) was placed in oil bath heated at 200~220°C beforehand, and the resulting chloroacetonitrile was distilled off at 80~100 mm. collected in a receiver chilled by a freezing mixture. Purification by further distillation gave a yield of 76%. ("Organic Syntheses": 61~70%).

the solvent furnished a yellow viscous residue which gave 2.6 g of Ia (28% yield), b. p. 140～145°C/1 mm. (literature[1]: b. p. 150°C/1 mm., 15% yield).

This compound has a characteristic odor of indolenine compound and solidified on standing to give m. p. 75～76°C after sublimation in vacuo.

Anal. Found: C, 78.41; H, 6.69; N, 15.17. Calcd. for $C_{12}H_{12}N_2$: C, 78.23; H, 6.57; N, 15.21%.

The picrate was recrystallized to give yellow crystals, m. p. 175～178°C. (literature[1]: 177～178°C).

Anal. Found: N, 16.99. Calcd. for $C_{12}H_{12}N_2 \cdot C_6H_3O_7N_3$: N, 16.94%.

2,3-Dimethyl-3-benzylindoline.—To a stirred solution of 1.8 g. of Ib in 25 cc. of absolute ethanol, 2.1 g. of sodium was added in five portions. After the sodium disappeared, water was added and the reaction mixture was extracted with ether. The ether extract gave, after removal of the solvent, 1.8 g. of crystals which melted at 80～82°C after recrystallization from ethanol-water. I. R. spectrum[17]: 3.10 μ (NH). U. V. spectrum[17]: λ_{max} 273 mμ (log ε 3.35) in ethanol.

Anal. Found: C, 85.86; H, 8.10. Calcd. for $C_{17}H_{19}N$: C, 86.03; H, 8.07%.

The picrate was recrystallized to yield yellow needles, m. p. 177～179°C.

Anal. Found: C, 58.86; H, 4.87. Calcd. for $C_{17}H_{19}N \cdot C_6H_3O_7N_3$: C, 59.22; H, 4.75%.

1,2-Dehydro-2-ethoxy-9-methyldinordesoxyeseroline (IV).—*By the action of ethanolic hydrochloric acid on Ia.*—A solution of 4.35 g. of Ia in 45 cc. of absolute ethanol was cooled at −10°C, and saturated with dry hydrogen chloride. After the solution was kept at room temperature overnight, ethanol was removed by distillation in vacuo, and the residue was neutralized with 5% sodium carbonate solution to afford crystals, m. p. 151～152°C (4.2 g.) after recrystallization from water-ethanol. I. R. spectrum: 3.2 μ (NH), 6.33 μ (CN). U. V. spectrum: λ_{max} 240 mμ (log ε 3.77), 294 mμ (log ε 3.35) in methanol.

Anal. Found: C, 72.85; H, 7.70; N, 12.25. Calcd. for $C_{14}H_{18}ON_2$: C, 73.01; H, 7.80; N, 12.17%.

The picrate was recrystallized to give yellow needles, m. p. 174～175°C.

Anal. Found: C, 52.95; H, 4.96; N, 15.09. Calcd. for $C_{14}H_{18}ON_2 \cdot C_6H_3O_7N_3$: C, 52.28; H, 4.61; N, 15.25%.

By the action of sodium ethoxide on Ia.—To a solution of sodium ethoxide prepared from 0.2 g. of sodium and 20 cc. of absolute ethanol, 0.38 g. of Ia was added with 1 cc. of ethanol. After the solution was refluxed for 1 hr., the reaction mixture was subjected to steam distillation, but 2,3-dimethylindole could not be detected in the steam distillate.

The residue of the steam distillation afforded a pale yellow precipitate which was purified by recrystallization from ethanol-water to give crystals, m. p. 148～149°C, undepressed m. p. on admixture with that prepared by the method described above.

Reductive Cleavage of IV with Potassium and *tert*-Butanol.—To a solution of 0.8 g. of IV in 30 cc. of *tert*-butanol, 1.8 g. of potassium was added in small portions. After the solution was refluxed on a water bath for 2 hr., the reaction mixture was subjected to steam distillation. The crystals which separated on the condenser weighed 0.2 g., and melted at 101～104°C after recrystallized from petroleum ether (b. p. 50～70°C). This compound was proved identical with 2,3-dimethylindole by the mixed m. p. (101～103°C) with an authentic specimen (m. p. 104～105°C).

Anal. Found: C, 82.81; H, 7.42; N, 9.41. Calcd. for $C_{10}H_{11}N$: C, 82.72; H, 7.64; N, 9.65%.

Ethyl 2,3-Dimethylindolenine-3-acetate (V).—Ia (4.6 g.) was ethanolyzed by boiling with 20 cc. of 94% ethanol and 10 cc. of concentrated sulfuric acid for 8 hr. The cooled reaction mixture was poured onto a stirred solution of 40g. of sodium carbonate in 100 cc. of water and 100 cc. of ether which formed an upper layer. The ether extract, after being washed with water and dried over magnesium sulfate, was concentrated to give a yellow brown liquid which was distilled to afford 4.2 g. of pale yellow viscous oil with green-yellowish fluorescence, b. p. 120～130°C/6 mm. I. R. spectrum: 5.75 μ (ester carbonyl), 6.30 μ (indolenine C=N). U. V. spectrum: λ_{max} 259 mμ (logε 3.75), λ_{min} 235 mμ (log ε 3.49) in ethanol.

Anal. Found: N, 6.01. Calcd. for $C_{14}H_{17}O_2N$: N, 6.06%.

The picrate was recrystallized to furnish yellow needles, m. p. 141～143°C.

Anal. Found: C, 52.47; H, 4.61; N, 12.22. Calcd. for $C_{14}H_{17}O_2N \cdot C_6H_3O_7N_3$: C, 52.17; H, 4.38; N, 12.17%.

Reductive Cleavage of V.—To a solution of 0.589 g. of V in 13 cc. of absolute ethanol, 1.0 g. of sodium was added in three portions as rapidly as the capacity of the condenser allowed, and after the disappearence of sodium the solution was heated on a water bath for 30 min. To the reaction mixture, 20 cc. of water was added and ethanol was removed to give a turbid solution from which a crystalline material (0.14 g.) precipitated. After recrysallization from petroleum ether (b. p. 50～70°C), this crystal showed m. p. 97～100°C, the identity of which with 2,3-dimethylindole was established by mixed m. p. determination with an authentic sample. Its picrate melted at 152～153°C alone and admixed with an authentic specimen.

Ethyl 2,3-Dimethylindoline-3-acetate (VI).—On catalytic hydrogenation of V (2.1 g.) with 69 mg. of platinum oxide in 10 cc. of acetic acid, the theoretical hydrogen up-take was completed after 2 hr. After the catalyst was filtered, the filtrate was poured onto a solution of 20 g. of sodium carbonate in 150 cc. of water, and extracted with ether. The ether extract,

17) Cf. M. Nakazaki and S. Isoe, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nipon Kagaku Zasshi*), **76**, 1161 (1955).

18) After the nomenclature of "The Ring Index", p. 196, this can be named as 3a, 8a-dihydro-1,2-dehydro-2-ethoxypyrrolo [2.3-b] indole.

after removal of the solvent, afforded a pale yellow oil, which gave 1.64 g. of (78% yield) VI, b. p. 153~154°C/6 mm. No fluorecence was observed. I. R. spectrum: 2.95 μ (NH), 5.76 μ (ester carbonyl). U. V. spectrum: λ_{max} 288 mμ (log ε 3.26), 248 mμ (log ε 3.82) in ethanol.

Anal. Found: C, 70.96; H, 8.24; N, 5.84. Calcd. for $C_{14}H_{19}O_2N$: C, 72.07; H, 8.21; N, 6.00%.

The picrate was recrystallized from ethanol to give yellow needles, m. p. 153°C.

Anal. Found: C, 51.95; H, 4.85; N, 12.12. Calcd. for $C_{14}O_{19}O_2N \cdot C_6H_3O_7N_3$: C, 51.95; H, 4.80; N, 12.12%.

The Action of Potassium *tert*-Butoxide on VI.—To a solution of potassium *tert*-butoxide prepared from 0.08 g. of potassium and 6 cc. of *tert*-butanol, a solution of 0.33 g. of VI in 2 cc. of *tert*-butanol was added. After the reaction mixture was heated for 1 hr. on a water bath, the solvent was removed under reduced pressure. After the residue was dissolved in water and saturated with sodium chloride, the solution was extracted with ether. The ether extract was shaken with 2 N hydrochloric acid solution to separate neutral and basic fractions. From the ether layer, after the usual work-up, there could not be detected anything but a faint smell of *tert*-butanol. The hydrochloric acid solution was made strongly basic, and the separated oily material was extracted with ether. The ether extract gave, after evaporation of the solvent, 0.25 g. of liquid which was converted into picrate directly. The crude picrate melted at 145~151°C with a little effervescence, but after two more recrystallizations from ethanol, its m. p. was 152~153°C and proved identical with the picrate of VI.

The Action of Sodium on the Ethanolic Solution of VI.—To a solution of 0.47 g. of VI in 9 cc. of absolute ethanol, 0.7 g. of sodium was added in three portions. After the sodium disappeared, the solvent was removed on a water bath, and water was added to the residue. The basic and neutral fractions were separated as mentioned above. From the neutral fraction, no 2,3-dimethylindole was found. The basic fraction gave 0.221 g. of a pale yellow liquid which afforded a yellow prismatic picrate melting at 152~154°C after recrystallization from ethanol. The mixed m. p. with the picrate of VII (m. p. 151~153°C) was 151~154°C.

Anal. Found: C, 51.84; H, 5.16; N, 13.23. Calcd. for $C_{12}H_{17}ON \cdot C_6H_3O_7N_3$: C, 51.42; H, 4.80; N, 13.33%.

β-(2, 3-Dimethylindolinyl)-ethanol (VII).—To a suspension of 0.15 g. of lithium aluminum hydride on 20 cc. of absolute ether, a solution of 0.909 g. of VI in 10 cc. of ether was added dropwise over a period of 30 min. After the reaction mixture was heated on a water bath for 1 hr., the excess of the reduction reagent was destroyed by the addition of ethyl acetate, and the resulting white voluminous precipitate was dissolved in 2N sodium hydroxide. Continuous extraction with ether (10 hr.) gave, after removal of the solvent, 0.635 g. of a viscous liquid, which was distilled at 136~145°C (air bath temperature) under 3 mm. to yield 0.53 g. of viscous oil. This solidified to give colorless needles, m. p. 100~101°C, after recrystallization from ethanol-petroleum ether.

Anal. Found: C, 75.63; H, 9.14; N, 7.38. Calcd. for $C_{12}H_{17}ON$: C, 75.35; H, 8.96; N, 7.32%.

The picrate was recrystallized to produce yellow crystals, m. p. 151~153°C.

2-Methyltryptophol (VIII).—To a slurry of 1.75 g. lithium aluminum hydride in 130 cc. of absolute ether, a mixture of 10 g. of ethyl 2-methylindole-3-acetate[19] in 50 cc. of ether was added dropwise at such a rate as to keep the ether boiling.

Stirring and refluxing was continued for 30 min., and 15 cc. of ethyl acetate was added to destroy the excess of the reduction reagent followed by the addition of dilute sulfuric aid. The aqueous layer was thoroughly extracted with ether, and ether extract was washed with water and dried over anhydrous magnesium sulfate. After the removal of the solvent, the ether extract gave a viscous liquid, which was purified by distillation in vacuo resulting in 6.0 g. of liquid (75% yield), b. p. 143~144°C/10^{-3} mm.[20]

3a, 8a-Dihydro-3a, 8a-dimethyl-2-furo(2.3-b)-indole (X).—A solution of 5 g. of VIII in 30 cc. of ether was added dropwise onto a stirred cold Grignard solution prepared from 2.08 g. of magnesium and 15.3 g. of ethyl iodide in 15 cc. of ether.

After being kept at room temperature for about 20 min., the reaction mixture was refluxed on a water bath for 1 hr. To this solution 9.3 g. of methyl iodide was added during 3 hr., and the mixture was kept at room temperature overnight. The Grignard complex was decomposed with acetic acid and water, and extracted with ether. From the ether extract the basic material was transferred into 1 N hydrochloric acid. The oily material, liberated by the addition of 2 N sodium hydroxide solution to the hydrochloric acid extract, was again extracted with ether. Distillation of the residue, after evaporation of ether, at a reduced pressure gave 0.94 g. of viscous oil, b. p. 125~126°C/5 mm.

This compound solidified gradually, and recrystallization from petroleum ether (b. p. 50~70°C) gave prismatic crystals, m. p. 51.5~52.5°C. I. R. spectrum: 3.00 μ (NH). U. V. spectrum: λ_{max} 245 mμ (log ε 3.7), 293 mμ (log ε 3.0).

Anal. Found: C, 76.29; H, 8.26. Calcd. for $C_{12}H_{15}ON$: C, 76.15; H, 7.99%.

The picrate gave yellow prisms from ethanol, m. p. 137~139°C.

Anal. Found: C, 52.01; H, 4.61; N, 13.39. Calcd. for $C_{12}H_{15}ON \cdot C_6H_3O_7N_3$: C, 51.67; H, 4.34; N, 13.39%.

The Action of Sodium on the Ethanolic Solution of X.—One gram of sodium was added in three portions to a solution of 0.26 g. of X in

19) M. V. Bulloch and S. W. Fox, *J. Am. Chem. Soc.*, **73**, 5156 (1951).

20) T. Hoshino and K. Shimodaira, *Ann.*, **520**, 19 (1935) prepared this alcohol by the Bouveault-Blanc reduction in a yield of 32%, b. p. 198°C/3.5 mm. and m. p. 55~56°C.

20 cc. of absolute ethanol. After the reaction was complete, water was added to the reaction mixture and saturated with sodium chloride. The solution was thoroughly extracted with ether, but the test of 2,3-dimethylindole was negative on the small amount of residue remaining after removal of the solvent.

Reductive Cleavage of Ia. Isolation of Ethylamine.—In a 100 cc. three-necked flask, provided with an inlet tube for dry nitrogen, a reflux condenser carrying a glass tubing which reached the bottom of a Erlenmeyer flask containing 10 cc. of 4 N hydrochloric acid solution, and an inlet tude for sodium, were placed 2.09 g. of Ia and 45 cc. of absolute ethanol. While nitrogen from a cylinder was passed through the flask, 3.5 g. of sodium was added in five portions as rapidly as the capacity of the condenser allowed. Volatile material was swept with nitrogen gas into the hydrochloric acid solution. After completion of the reaction, cooling water for the condenser was cut off, and about 5 cc. of ethanol was distilled through the condenser into the Erlenmeyer flask contaning the acid solution. Another 15 cc. of ethanol was distilled into the same receiver by the usual downward distillation.

Water was added to the residue which remained in the three-necked flask and the turbid solution was distilled with steam. From the distillate, 0.5 g. of 2, 3-dimethylindole was obtained, and identified by mixed m. p. determination with an authentic sample and as in the form of picrate.

The hydrochloric acid solution containing the basic material, was concentrated in vacuo to give a crystalline product which was soluble completely in absolute ethanol. The amine generated by the addition of 10 cc. of 4 N sodium hydroxide solution onto the above mentioned amine hydrochloride, was distilled with water into a flask containing 0.2 g., of diethyl oxalate and 1 cc. of water. The crystals separated from the cold solution, were washed with a small amount of cold water and dried in a desiccator to give 10 mg. of colorless needles, m. p. 178~179°C, which did not depress the mixed m. p. with an authentic sample of ethyloxamide (m. p. 178~180°C[21]). Their I. R. spectra could overlap in every respect.

Anal. Found: C, 50.28; H, 8.85: N, 19.40. Calcd. for $C_6H_{12}O_2N_2$: C, 49.98; H, 8.39; N, 19.43%.

On a control experiment using the same method, 65 mg. of ethyloxamide was isolated by the reduction of 600 mg. of acetonitrile with sodium-ethanol.

The author is very gratiful to Messrs. Kohei Tanno, Masaru Tamura and Munesuke Sato for their skillful technical assistance.

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21) S. P. Mulliken, "A Method for the Indentification of Pure Organic Compounds," Vol. II, John Wiley Inc., New York (1922), p. 132.

Indirect Complexometric Titration of Beryllium with Ethylenediaminetetraacetic Acid

By Seizo MISUMI and Tomitsugu TAKETATSU

(Recived December 19, 1958)

Ethylenediaminetetraacetic acid (EDTA) has been used for volumetric determination of various metal ions, but it can not be used for a direct titration of the beryllium ion nor for that of the sodium and the potassium ion because these metal ions do not form stable EDTA complexes. Flaschka[1] reported the indirect titration method for sodium, and Pilleri[2] and one of the present authors[3] that for potassium. Pirtea and Mihail[4] reported that beryllium was determined gravimetrically, producing the precipitate $[Co(NH_3)_6]\cdot[(H_2O)_2Be_2(CO_3)_2(OH)_3]\cdot 3H_2O$, by adding saturated hexammine cobaltic trichloride solution (Luteo salt) to beryllium carbonate solution. We studied the determination of beryllium ion concentration by volumetrically measuring the cobalt content in this precipitate. This method was proved to be quantitative and it was possible to separate and determine beryllium from iron (III), aluminum

1) H. Flaschka, *Mikrochemie ver. Mikrochim. Acta*, **39**, 391 (1952).
2) R. Pilleri, *Z. anal. Chem.*, **157**, 1 (1957).
3) T. Taketatsu, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **76**, 756 (1957).
4) T. I. Pirtea and G. Mihail, *Z. anal. Chem.*, **159**, 205 (1958).

and magnesium by using EDTA as a masking agent.

Experimental

Reagents.—Standard beryllium solution was prepared by dissolving the nitrate salt in distilled water and the concentration was determined gravimetrically as the oxide. The content (BeO) was 1.95 mg./ml.

Standard EDTA solution was obtained by dissolving the pure disodium salt of ethylenediaminetetraacetic acid dihydrate (Research Laboratory, Dojindo & Co., Ltd.) in distilled water. The concentration was determined by titrating standard zinc chloride solution with Eriochrome black T as indicator. The concentration was 0.01016 mol.

Hexammine cobaltic trichloride (Luteo salt) solution was prepared by Fernelius's method[5] and the supernatant liquid of the saturated solution was used in this experiment.

All other chemicals used were analytical reagent grades.

General Procedure.—An excess of ammonium carbonate was added to about 10 ml. of a slightly acidic solution containing 0.70 to 3.50 mg. of beryllium; a precipitate of basic beryllium carbonate was formed, which was then dissolved completely by stirring for a time. To this clear solution was added a few milliliters of saturated Luteo salt solution and an orange yellow precipitate[4] was obtained by stirring the solution. The solution containing the precipitate was stirred occasionally by a magnetic stirrer for several hours to make the precipitation complete. The precipitate was then filtered with a glass filter (1G. No. 4) and washed 2 to 3 times successively with 2 to 3 ml. of the following solutions: 0.2% Luteo salt solution, a mixture of ethanol and water (60 ml. +40 ml.) containing 2 to 3 drops of 0.2% Luteo salt solution, and absolute ethanol. The percipitate on the glass filter was dissolved in a small amount of 0.1 N hydrochloric acid. To decompose the Luteo salt in the solution obtained, one gram of sodium hydroxide was added to the solution and then the solution was boiled till the black-brown precipitate of cobalt (III) hydroxide was obtained. The solution containing the precipitate was acidified by adding hydrochloric acid and boiled to dissolve the cobalt hydroxide. By this procedure the valency of cobalt was reduced to II from III with hydrochloric acid and a solution containing cobalt (II) and beryllium ions was obtained. After the solution cooled, a small amount of malic acid was added to the solution and it was neutralized with aqueous ammonia (1:1, by volume). The cobalt in the solution was titrated with the standard EDTA solution by adding 0.2 g. of Murexide as indicator. The point at which the indicator attained its maximum violet color was as the end point.

1 ml. of 0.01 mol. EDTA solution
≡0.1803 mg. of berlliyum.

These procedures were carried out at 20~25°C except for boiling purposes.

Results and Discussion

In the general procedure described above, the following factors were specially considered; effects of the amount of ammonium carbonate, Luteo salt and malic acid, and of time allowed for the formation of the precipitate II*.

1) Relation between Ammonium Carbonate Added and the Time Required to Dissolve Basic Beryllium Carbonate.—When an excess of ammonium crabonate was added to about 10 ml. of solution containing 1.40 mg. of beryllium, basic beryllium carbonate was precipitated at first, but the precipitate was dissolved gradually by stirring, because beryllium carbonate complex was produced. The relation between the amount of ammonium carbonate added and the time required for dissolving the precipitate was studied and the results are shown in Table I. It is shown that the more the amount of ammonium carbonate, the shorter the time required for the dissolving of the precipitate.

TABLE I. RELATION BETWEEN THE AMOUNT OF AMMONIUM CARBONATE AND APPROXIMATE TIME REQUIRED TO DISSOLVE BASIC BERYLLIUM CARBONATE

Ammonium carbonate added, g.	Time for dissolving the precipitate, min.
0.5	>60
1.0	25~30
1.5	10~20
2.0	7~ 8
2.5	5~ 7
3.0	3~ 5
4.0	1~ 2

2) Effect of Luteo Salt Added.—To determine the optimum amount of Luteo salt added, various volumes of saturated Leuteo salt solution were added to the beryllium carbonate complex solution. In this case, all other conditions were kept constant. The results are shown in Table II.

It was found that the amount of the reagent added did not affect the determination of beryllium within the range 1 to 8 ml.

5) W. C. Fernelius, "Inorganic Syntheses", Vol. II, McGraw Hill Book Co., Inc., New York (1946), p. 217.

* The precipitate II means $[Co(NH_3)_6][(H_2O)_2Be_2(CO_3)_2(OH)_2]\cdot 3H_2O$

TABLE II. EFFECT OF LUTEO SALT ADDED

Be taken, mg.	Saturated Luteo salt solution added, ml.	Vol. of 0.01016 mol. EDTA titrated, ml.	Be found, mg.	Error, mg.
1.40	1.0	7.72	1.41	+0.01
1.40	2.0	7.79	1.43	+0.03
1.40	4.0	7.61	1.39	−0.01
1.40	5.0	7.72	1.41	+0.01
1.40	8.0	7.65	1.40	±0.00

3) Relation between the Amount of the Precipitate and That of Ammonium Carbonate Added.—Since the amount of ammonium carbonate added had an effect on the formation of the precipitate II., the relation between the amount of the precipitate formed and that of ammonium carbonate added was studied at various time intervals after Luteo salt was added. The results are shown in Fig. 1.

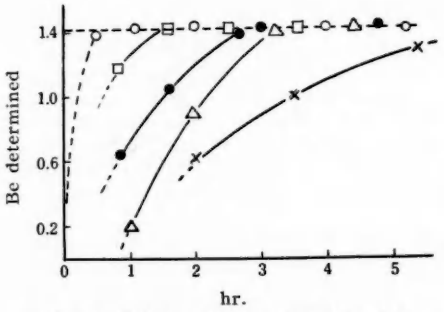

Fig. 1. Relation between beryllium determined v.s. time at various concentrations of ammonium carbonate added.

Ammoium carbonate	
—○—○—	1.0 g
—□—□—	1.5 g
—●—●—	2.0 g
—△—△—	3.0 g
—×—×—	4.0 g

When a small amount of ammonium carbonate had been added to the initial beryllium solution, the precipitate II was formed quantitatively as soon as Luteo salt was added. On the other hand, a longer time was necessary for the formation of the precipitate II with increase in the amount of ammonium carbonate. However, as it is convenient for the dissolution of the precipitate of basic beryllium carbonate to add a greater amount of ammonium carbonate as described above, 1.5 to 2.0 g. of ammonium carbonate was used in this experiment.

4) Effect of Malic Acid on the Titration of Cobalt. — When the titration of cobalt was carried out in an ammonium alkaline solution by using Murexide as indicator, beryllium precipitated as its hydroxide and the results, therefore, proved inaccurate. Since the hydroxide does not precipitate in general in the presence of malic acid, the effect of malic acid on the titration of cobalt was studied. The results are shown in Table III.

TABLE III. EFFECT OF MALIC ACID ADDED

Co taken, mg.	5% malic acid added, ml.	Vol. of 0.01016 mol. EDTA titrated, ml.	Co found, mg.	Error, mg.
3.64	0	6.08	3.64	±0.00
3.64	2	6.08	3.64	±0.00
3.64	4	6.08	3.64	±0.00
3.64	5	6.07	3.63	−0.01
3.64	10	6.05	3.62	−0.02

It is evident that the addition of 2 to 10 ml. of 5% malic acid solution did not give an error in the titration. But larger amounts of malic acid showed negative errors. Therefore, 2 ml. of 5% malic acid were used.

The results obtained from the titration of cobalt (3.64 mg.) with standard EDTA solution in the presence of 0.70 to 3.50 mg. of beryllium and 2 ml. of 5% malic acid are shown in Table IV. It was found that beryllium gives no effects in the titration of cobalt.

TABLE IV. TITRATION OF COBALT IN THE PRESENCE OF BERYLLIUM

Co taken, mg.	Be added, mg.	Vol. of 0.01016 mol. EDTA titrated, ml.	Co found, mg.	Error, mg.
3.64	0.70	6.08	3.64	±0.00
3.64	1.40	6.07	3.63	−0.01
3.64	1.40	6.09	3.65	+0.01
3.64	2.10	6.08	3.64	±0.00
3.64	3.50	6.07	3.63	−0.01

The optimum conditions for the general procedure were concluded as follows: the amount of ammonium carbonate added, 1.5 to 2.0 g.; the volume of saturated Luteo salt solution added, 2 ml.; the time allowed for the precipitate II to form, about 3 hr. after Luteo salt was added; the volume of 5% malic acid added, 2 ml.

5) Determination of Various Concentrations of Beryllium under the Optimum Conditions. — Various concentrations of

beryllium were determined by following the general procedure under the optimum conditions and the results are shown in Table V. Thus, it was concluded that the indirect titration of beryllium was satisfactorily carried out.

TABLE V. DETERMINTION OF VARIOUS CONCENTRATIONS OF BERYLLIUM AT THE OPTIMUM CNDITIONS

Be taken, mg.	Vol. of 0.01016 mol. EDTA titrated, ml.	Be found, mg.	Error, mg.
0.70	3.90	0.71	+0.01
0.70	3.84	0.70	±0.00
1.40	7.63	1.40	±0.00
1.40	7.68	1.41	+0.01
2.10	11.36	2.08	−0.02
3.50	19.02	3.48	−0.02

6) The Determination in the Presence of Iron (III), Aluminum and Magnesium. — After EDTA solution (0.1 mol., 5 ml.) and ammonium chloride (0.5 g.) were added to the sample solution containing iron(III), aluminum and magnesium, aqueous ammonia (1 : 1, 1 ml.) was added to the solution. At that time only beryllium hydroxide was precipitated. Then, 2 g. of ammonium carbonate was added to the solution and beryllium hydroxide was dissolved by stirring. The subsequent determination of beryllium was carried out by the procedure described above. In this case, iron, aluminum and magnesium were completely separated from beryllium when the precipitate II was formed and filtered. The results are shown in Table VI.

It is shown that the determination of berylium in the presence of these metals was carried out satisfactiorily. Therefore, this procedure is considered useful for a practical analysis of beryllium.

TABLE VI. DETERMINATION OF BERYLLIUM IN THE PRESENCE OF IRON(III), ALUMINUM AND MAGNESIUM

Be taken, mg.	Other metals added.	mg.	Vol. of 0.01016 mol. EDTA titrated, ml.	Be found, mg.	Error, mg.
1.40	Fe^{3+}	2.0	7.70	1.41	+0.01
1.40	Fe^{3+}	4.0	7.60	1.39	−0.01
1.40	Fe^{3+}	8.0	7.58	1.39	−0.01
1.40	Al^{3+}	1.7	7.64	1.40	±0.00
1.40	Al^{3+}	3.4	7.60	1.39	−0.01
1.40	Al^{3+}	6.8	7.55	1.38	−0.02
1.40	Mg^{2+}	2.1	7.65	1.40	±0.00
1.40	Mg^{2+}	8.3	7.69	1.41	+0.01

Summary

When Luteo salt was added to beryllium carbonate complex solution, the precipitate $[Co(NH_3)_6][(H_2O)_2Be_2(CO_3)_2(OH)_3]\cdot 3H_2O$ was obtained. In this experiment, the indirect determination of beryllium was tried by the titration of the cobalt content in the precipitate with EDTA. The following procedures were examined mainly; the formation of the precipitate II, the decomposition of the precipitate and titration of cobalt in the presence of beryllium. In the optimum conditions, 0.70 to 3.50 mg. of beryllium were determined quantitatively. This method could be applied to separation and determination of beryllium from iron(III), aluminum and magnesium by using EDTA as a masking agent.

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Molecular Rotations of Glucides in Relation to their Structures. VII.[1] *Internal Conformation of $O^{1\alpha}$—C^{m} Bond in $(OCH_3)^{1\alpha}$ of Methyl α-D-Xylopyranoside and of Methyl β-L-Arabinopyranoside in Aqueous Solutions*[2]

By Shukichi YAMANA

(Received October 21, 1958)

Although the internal conformation of $O^{1\alpha}$—C^{m} bond[3] in $(OCH_3)^{1\alpha}$ of methyl α-D-xylopyranoside[5,6] or of methyl β-L-arabinopyranoside[6,7] in crystalline state has been studied from the standpoint of X-ray analysis, those in the aqueous solutions have not yet been determined owing to the lack of a suitable method. (Fig. 1)

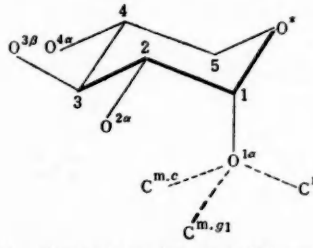


Fig. 1. Perspective drawing of the molecular model of methyl α-D-xylopyranoside: *t—trans* ($\phi_{1\alpha}=0°$), *g1—gauche* 1 ($\phi_{1\alpha}=120°$), *c—cis* ($\phi_{1\alpha}=180°$).

Hudson empirically observed the existence of a certain quantitative relationship between the structure of methyl glycosides and their molecular rotations, $[M]_D^{20}(W)$[8], but no one has attempted to utilize these $[M]_D^{20}(W)$ values for the determination of the internal conformation of their $O^{1\alpha}$—C^{m} bonds. Recently, the present author succeeded in presuming the internal conformation of C^{6}—O bond in D-mannopyranose in its aqueous solution by using $[M]_D^{20}(W)$ values of some glucides[9]. By a similar method, the internal conformation of $O^{1\alpha}$—C^{m} bond in $(OCH_3)^{1\alpha}$ of methyl α-D-xylopyranoside and of methyl β-L-arabinopyranoside in aqueous solutions has been presumed in this article.

Molecular Model and Data Used.—As the molecular model, the one proposed by McDonald and Beevers was used. The values of bond lengths and valency angles concerning the side chain are assumed as follows; $O^{1\alpha}$—C^{m} is 1.421 Å[a] and $\angle C^{1}O^{1\alpha}C^{m}$ is a tetrahedral angle (109° 28′). The unit groups in the glucide molecules under discussion and their corresponding molecular rotations are given in Table I.

As the optical data for OH, CH_3 and H, the values used in the previous papers[1,4]

TABLE I

Name	Unit groups	$[M]_D^{20}(W)$	Lit.
methyl α-D-xyloside	$[(OCH_3)^{1\alpha}$,[10] $(OH)^{2\alpha}$, $(OH)^{3\beta}$, $(OH)^{4\alpha}$, Ring]	252.6°	(b)
methyl β-L-arabinoside	$[(OCH_3)^{1\alpha}$, $(OH)^{2\alpha}$, $(OH)^{3\beta}$, $(OH)^{4\beta}$, Ring]	403.0°	(c)
α-D-xylose	$[(OH)^{1\alpha}$, $(OH)^{2\alpha}$, $(OH)^{3\beta}$, $(OH)^{4\alpha}$, Ring]	140.5°	(b)
β-L-arabinose	$[(OH)^{1\alpha}$, $(OH)^{2\alpha}$, $(OH)^{3\beta}$, $(OH)^{4\beta}$, Ring]	286.1°[11]	(c)

1) Part VI; S. Yamana, This Bulletin, **31**, 564 (1958).

2) Reported at the Symposium on the Structural Chemistry, held on October 13, 1958, at Kyoto, under the auspices of the Chemical Society of Japan.

3) $O^{1\alpha}$ means the O atom which combines with C^{1}-atom of the aldopyranose-ring in α-orientation, and so on. (Cf. the foot-note *5 in the previous paper[4]). C^{m} means the C atom in methyl group. Then, $O^{1\alpha}$—C^{m} bond is the O—C bond in $(OCH_3)^{1\alpha}$. (Ref. Fig. 1).

4) S. Yamana, This Bulletin, **30**, 203 (1957).

5) E. G. Cox, *J. Chem. Soc.*, **1932**, 2535.

6) H. Braekken, C. J. Koren and N. A. Sörensen, *Z. Krist.*, **88**, 205 (1934).

7) E. G. Cox and T. H. Goodwin, **85**, 462 (1933); E. G. Cox, T. H. Goodwin and (Miss) A. I. Wagstaff, *J. Chem. Soc.*, **1935**, 978.

8) C. S. Hudson, *J. Am. Chem. Soc.*, **31**, 66 (1909).

9) S. Yamana, This Bulletin, **30**, 920 (1957).

a) D. G. Burkhard and D. M. Dennison. *Phys. Rev.*, **84**, 408 (1951).

10) The internal conformation of $O^{1\alpha}$—C^{m} bond in $(OCH_3)^{1\alpha}$ of methyl α-D-xyloside is the same as that of methyl β-L-arabinoside. Concerning this information, refer to "**Method Proposed**" in this article.

b) F. J. Bates and Associates, "Polarimetry, Saccharimetry and the Sugars", United States Government Printing Office, Washington (1942), p. 759.

c) Ibid., p. 708.

11) Hudson's datum is 303.3°. (Ref. the foot-note *12 in the previous paper[12].)

12) S. Yamana, This Bulletin, **31**, 558 (1958).

are again adopted in this article. In order to simplify the calculations, the optical centers of OH and CH_3 groups are assumed to be located at O and C atoms, respectively[13]. Accordingly, the value of ζ_{CH_3} becomes 0.2880 $(3/n^2+2)^{1/2}$ [14]. The refractive indices of the aqueous solutions of these methyl glycosides are presumed to be nearly equal to 1.34[15].

Method Proposed.—If the orientation of $(OH)^4$ in methyl β-L-arabinopyranoside is changed from β to α, methyl α-D-xylopyranoside is obtained[16]. But, throughout the course of this process, the distance between $(CH_3)^{\leftarrow 1\alpha}$ [17] and $(OH)^4$ is so much larger[18] than those between $(CH_3)^{\leftarrow 1\alpha}$ and the other atoms (than $(OH)^4$) in the same molecules, that the orientation-change of $(OH)^4$ should not cause any influence on the internal conformation of $O^{1\alpha}$—C^m bond. In other words, the internal conformation of $O^{1\alpha}$—C^m bond in $(OCH_3)^{1\alpha}$ of methyl α-D-xylopyranoside is said to be the same as that of methyl β-L-arabinopyranoside in their aqueous solutions. Then, the unit groups which can couple with $(OH)^4$ dynamically in the molecules of methyl α-D-xylopyranoside and of methyl β-L-arabinopyranoside are $(OCH_3)^{1\alpha}$, $(OH)^{2\alpha}$, $(OH)^{3\beta}$ and Ring[16]. Therefore, Yo. Diff.[20] between these two methyl glycosides is given by the following equation,

$$\{(4\alpha)-(4\beta)\}\lambda\{(OCH_3)^{1\alpha}+(2\alpha)+(3\beta)+R\}^{21)}=(4\alpha)\lambda(OCH_3)^{1\alpha}+(4\alpha)\lambda(2\alpha)+(4\alpha)\lambda(3\beta)+(4\alpha)\lambda R\}-\{(4\beta)\lambda(OCH_3)^{1\alpha}+(4\beta)\lambda(2\alpha)+(4\beta)\lambda(3\beta)+(4\beta)\lambda R\}\equiv I$$

Similarly, Yo. Diff. between α-D-xylopyranose and β-L-arabinopyranose is given by,

$$\{(4\alpha)-(4\beta)\}\lambda\{(1\alpha)+(2\alpha)+(3\beta)+R\}=\{(4\alpha)\lambda(1\alpha)+(4\alpha)\lambda(2\alpha)+(4\alpha)\lambda(3\beta)+(4\alpha)\lambda R\}-\{(4\beta)\lambda(1\alpha)+(4\beta)\lambda(2\alpha)+(4\beta)\lambda(3\beta)+(4\beta)\lambda R\}\equiv J$$

Accordingly, $I-J$[22]$=\{(4\alpha)\lambda(OCH_3)^{1\alpha}-(4\beta)\lambda(OCH_3)^{1\alpha}\}-\{(4\alpha)\lambda(1\alpha)-(4\beta)\lambda(1\alpha)\}=(4\alpha)\lambda(OCH_3)^{1\alpha}-(4\beta)\lambda(OCH_3)^{1\alpha}\}-\{(4\alpha)\lambda(OH)^{1\alpha}-(4\beta)\lambda(OH)^{1\alpha}\}$[23] (1)

$(OCH_3)^{1\alpha}$ may be considered to occur by replacing $H^{\leftarrow 1\alpha}$-atom[25] in $(OH)^{1\alpha}$ by $CH_3^{\leftarrow\alpha}$ group. And because of the small polarizability of $H^{\leftarrow 1\alpha}$, $(4\alpha)\lambda H^{\leftarrow 1\alpha}\simeq 0$ and $(4\beta)\lambda H^{\leftarrow 1\alpha}\simeq 0$. Therefore, Eq. 1 can be simplified as below;

$$I-J=[(4\alpha)\lambda\{O^{1\alpha}+(CH_3)^{\leftarrow 1\alpha}\}-(4\beta)\lambda\{O^{1\alpha}+(CH_3)^{\leftarrow 1\alpha}\}]-[(4\alpha)\lambda\{O^{1\alpha}+H^{\leftarrow 1\alpha}\}-(4\beta)\lambda\{O^{1\alpha}+H^{\leftarrow 1\alpha}\}]\simeq(4\alpha)\lambda(CH_3)^{\leftarrow 1\alpha}-(4\beta)\lambda(CH_3)^{\leftarrow 1\alpha}$$ [26]

The value of this $\{(4\alpha)\lambda(CH_3)^{\leftarrow 1\alpha}-(4\beta)\lambda(CH_3)^{\leftarrow 1\alpha}\}$ was calculated by PM-method[27] as a function of $\phi_{1\alpha}$[19]. These values, $[\mu]^{20}_{D\,obs}$ for $(I-J)$ are shown in Table II.

The corresponding observed value of $(I-J)$, given by [{([M]$^{20}_D$(W) of methyl α-D-xylopyranoside) minus ([M]$^{20}_D$(W) of

13) In Eq. 5 of the previous paper[1], ζ_{CH3} was calculated as $0.1962\ (3/n^2+2)^{1/2}$ on the supposition that the optical center of CH_3 group is located at the center of mass of ^rC—(CH_3) bond (cf. the foot-note *13 of the previous paper[12]).) But here, since CH_3 group combines with O atom instead of ^rC-atom, the above value of ζ_{CH3} is hardly adoptable.

14) According to Hudson's data of L-arabinoses, $\zeta_{CH3}=0.6206(3/n^2+2)^{1/2}$. (Ref. the foot-note *31 in the previous paper[1]).

15) The refractive index (n) of an aqueous solution of methyl glycoside is 1.33~1.35[d]. When the value of n changes by 0.01, $(n^2+2/3)$ changes by $\partial/\partial n(n^2+2/3)\delta n\simeq 0.007$. The magnitude of this value of $(n^2+2/3)$-change is very small and may be neglected on comparison with that of $(n^2+2/3)\simeq 1.265$. On the other hand, $[\mu]^{20}_{D\,obs}$ contains the factor n in itself only in the form of $(n^2+2/3)$. (Ref. "**Theoretical Formulae**" in the previous paper[4].) Then, $[\mu]^{20}_{D,obs}$, resulting from the dynamical coupling between two definite unit groups may be considered to be constant in that range of $n=1.33\sim1.35$.

d) "International Critical Tables of Numerical Data", Vol. 7. p. 69.

16) Ref. Table I in this article.

17) $(CH_3)^{\leftarrow 1\alpha}$ indicates the CH_3 group which combines with $O^{1\alpha}$-atom, and so on. Therefore, $(CH_3)^{\leftarrow 1\alpha}$ is the CH_3 group in $(OCH_3)^{1\alpha}$. (Ref. Fig. 1).

18) Since C^1- and C^4-atoms are situated nearly on the opposite ends of a diameter of the aldopyranose-ring together, the distances between C^m-atom[3] in $(CH_3)^{\leftarrow 1\alpha}$ and the O atom in $(OH)^4$ are shown below:

	longest	shortest
$(OH)^{4\alpha}$	5.91 Å (at $\phi_{1\alpha}$[19]$=60°$)	3.63 Å (at $\phi_{1\alpha}=240°$)
$(OH)^{4\beta}$	5.60 Å (at $\phi_{1\alpha}=60°$)	4.23 Å (at $\phi_{1\alpha}=240°$)

19) The author defined an angle $\phi_{1\alpha}$ which determines the internal conformation of $O^{1\alpha}$—C^m bond as follows; (i) $\phi_{1\alpha}$ is zero at the situation where C^m— and C^2-atoms are in *trans* position each other. (ii) The value of rotation in the positive direction increases with the distance between C^4- and C^m-atoms. (Fig. 1).

20) Yo. Diff. is an abbreviated symbol of "yomeric difference". This is $[M]^{20}_D$(W)-change of a glucide, caused by the orientaionchange of $(OH)^4$ from β to α. (ref. the foot-note *10 in the previous paper[1].)

21) Ref. the foot-note *12 in the previous paper[1].

22) J is adopted only for the purpose of canceling the terms concerning the aldopyranose-ring, R, in I.

23) Ref. the foot-note *10 in the previous paper[24].

24) S. Yamana, This Bulletin, **30**, 916 (1957).

25) $H^{\leftarrow 1\alpha}$ means the H atom which combines with $O^{1\alpha}$-atom. (Cf. the foot-note 17 in this article).

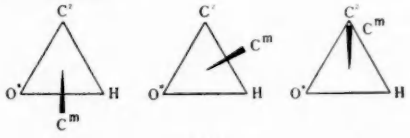
26) In other expressions, $(OCH_3)^{1\alpha}\simeq(OH)^{1\alpha}+(CH_3)^{\leftarrow 1\alpha}$
$\therefore$ Eq. $1=[(4\alpha)\lambda(OCH_3)^{1\alpha}-(4\beta)\lambda(OCH_3)^{1\alpha}]-[(4\alpha)\lambda(OH)^{1\alpha}-(4\beta)\lambda(OH)^{1\alpha}]\simeq[(4\alpha)\lambda\{(OH)^{1\alpha}+(CH_3)^{\leftarrow 1\alpha}\}-(4\beta)\lambda\{(OH)^{1\alpha}+(CH_3)^{\leftarrow 1\alpha}\}]-[(4\alpha)\lambda(OH)^{1\alpha}-(4\beta)\lambda(OH)^{1\alpha}]=(4\alpha)\lambda(CH_3)^{\leftarrow 1\alpha}-(4\beta)\lambda(CH_3)^{\leftarrow 1\alpha}$

27) Ref. the foot-note *17 in the previous paper[12].

TABLE II. $\Sigma[\mu]^{20}_{Dobs}$ FOR THE DIFFERENCE BETWEEN TWO YOMERIC DIFFERENCE *I* AND *J*, AS A FUNCTION OF $\phi_{1\alpha}$

$\phi_{1\alpha}$	Isbell and Pigman's data of L-arabinoses	Hudson's data[14] of L-arabinoses
0	5.7	12.2
20	4.5	9.7
40	2.8	5.9
60	1.3	2.8
80	−1.4	−3.0
100	−3.3	−7.2
120	−4.9	−10.5
140	−5.7	−12.3
160	−5.5	−11.9
180	−4.2	−9.1
200	−2.1	−4.6
220	−0.4	−0.8
240	0.0	0.1
260	−0.2	−0.4
280	0.7	1.5
300	2.8	6.1
320	4.9	10.5
340	5.9	12.6

methyl β-L-arabinopyranoside)} minus {([M]$^{20}_{D}$(W) of α-D-xylopyranose) minus ([M]$^{20}_{D}$(W) of β-L-arabinopyranose)}], becomes −4.8 on the basis of the Isbell and Pigman's data of L-arabinoses or 12.4 on the basis of the Hudson's data of L-arabinoses[16]. The former value coincides with the calculated value when $\phi_{1\alpha}$ is 120° or 180° as seen in the second column of Table II and the latter value coincides with that when $\phi_{1\alpha}$ is 0° as seen in the third column of Table II. It follows from this result that there are three possible internal conformations of $O^{1\alpha}$—C^m bond as figured in Fig. 2.



trans $\phi_{1\alpha}=0°$ (Hudson) — *gauche* 1 $\phi_{1\alpha}=120°$ (Isbell and Pigman) — *cis* $\phi_{1\alpha}=180°$ (Isbell and Pigman)

Fig. 2. Internal conformation along $O^{1\alpha}$—C^1 axis.

Discussion of the Results

Among the above three possibilities, it seems difficult for a *cis* form to exist owing to the repulsion between C^2-atom and $(CH_3)^{\leftarrow 1\alpha}$. The internal conformation under consideration, therefore, should be either a *trans*- or a *gauche* 1 form.

C^5—O*—C^1—$O^{1\alpha}$—C^m moiety in methyl α-D-xylopyranoside (Ref. Fig. 1) and also in methyl β-L-arabinopyranoside, is considered to be a kind of polyoxymethylene-chain. The internal conformation of a polyoxymethylene-chain along its C—O axis has been investigated by the methods of measuring the dipole moment, infrared spectrum, etc.[28,29] And it has been concluded that the most stable form of —C—O—C—O—C— chain is a *gauche* type[30]. From these facts, O*—C^1—$O^{1\alpha}$—C^m moiety in the methyl glycoside under discussion is likely to exist in the conformation which corresponds to $\phi_{1\alpha}=0°$. This leads to the following anticipation.

The position of the minimal potential of $O^{1\alpha}$—C^m bond corresponds to $\phi_{1\alpha}=0°$. (Anticipation 1)

On the other hand, C^2—C^1—$O^{1\alpha}$—C^m moiety in metyl α-D-xylopyranoside and in methyl β-L-arabinopyranoside is a kind of polyethyleneglycol-chain. Because of the non-polar property of its C—C bond and of the steric repulsion between two C-atoms in —C—C—O—C— chain, —C—C—O—C— along its C—O axis is strongly expected to be more stable in a *trans* form than in a *gauche* form. This produces the conclusion that the conformation under discussion would be more advantageous at $\phi_{1\alpha}=0°$ than at $\phi_{1\alpha}=120°$. In other words,

$O^{1\alpha}$—C^m bond has a tendency to keep the position corresponding to $\phi_{1\alpha}=0°$ rather than that corresponding to $\phi_{1\alpha}=120°$. (Anticipation 2)

This anticipation is consistent with Anticipation 1. Therefore, concerning [M]$^{20}_{D}$(W) of L-arabinoses, Hudson's data seem to be more reliable than Isbell and Pigman's data[31].

28) T. Uchida, Y. Kurita and M. Kubo, *J. Polymer Sci.*, **19**, 365 (1956).
29) A. R. Philpotts, D. O. Evans and N. Sheppard, *Trans. Faraday Soc.*, **51**, 1051 (1955).
30) Notice that the shape of a polyoxymethylene-chain shown by the word "*gauche* type" in this case is not the same as that of O*—C^1—$O^{1\alpha}$—C^m corresponding to the internal conformation of $O^{1\alpha}$—C^m bond of a *gauche* type in Figs. 1 and 2. O*—C^1—$O^{1\alpha}$—C^m moiety in Figs. 1 and 2 can become a *gauche* type of polyoxymethylene-chain when $\phi_{1\alpha}$ is 0° and become a *trans* type of polyoxymethylene-chain when $\phi_{1\alpha}$ is 120°. (Ref. Fig. 3).

Fig. 3. Polyoxymethylene-chain of *trans* type.

31) If Isbell and Pigman's data are correct, it must be concluded that the internal conformation of $O^{1\alpha}$—C^m bond corresponds to $\phi_{1\alpha}=120°$. In this case, a kind of the attractive force should be considered between $O^{2\alpha}$-atom and C^m-atom (strictly speaking, the H atom which is combined with C^m-atom).

Summary

By the author's new method, the internal conformation of $O^{1\alpha}—C^{m}$ bond in $(OCH_3)^{1\alpha}$ of methyl α-D-xylopyranoside and of methyl β-L-arabinopyranoside in aqueous solutions was presumed. At the same time, Isbell and Pigman's data and Hudson's data of $[M]_D^{20}(W)$ of L-arabinoses were discussed.

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On the Intramolecular Charge Transfer Spectra and Structure of Isomeric Aminopyridines

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In a series of papers, we have reported detailed theoretical studies on the electronic structure and the nature of electronic transitions of nitrogen heterocycles[1-5]. The detailed Hartree-Fock SCF study has been made only for nitrogen heterobenzenes such as pyridine[1], pyrazine[1], *sym*-triazine[1] and *sym*-tetrazine[2]. In addition, some extensions to larger molecules such as quinoline[3,5], isoquinoline[3,5], phthalazine[5], quinoxaline[5], acridine[4,5] and phenazine[4,5] have been made on the basis of the results obtained for nitrogen heterobenzenes, employing the perturbation method based on the Hartree-Fock SCF theory. Thus a theoretical ground for the classification and interpretation of the electronic spectra of nitrogen heterocycles has been given. As an extension of these investigations, we have studied the electronic structure and the spectra of some substituted nitrogen heterocycles. Among these, we have taken up the isomeric aminopyridines. There have been some disputes concerning the molecular forms of these molecules, especially 2- and 4- aminopyridines, i.e., imine-enamine tautomerism[6]. However, the possibility of the existence of imino-form was rejected by Anderson and Seeger[7] by spectral studies of these and related molecules and also Angyal and Angyal[8] reported that these compounds exist predominantly in the amino-form by critically surveying the foregoing data and arguments and also by the measurement of pK_a values of these molecules and related ones. Nevertheless, there seem to remain some ambiguities about this problem, even now. Morita[9] has calculated the electronic spectra of 4-aminopyridine by a method analogous to Dewar and Paoloni[10], assuming various models with respect to the molecular forms of this molecule. However, no definite conclusion about the form of this molecule has been derived from his calculation. We have tried to make clear the interrelation among the isomeric aminopyridines and their relation to aniline, pyridine and benzene, with respect to the electronic structure and spectra. We have assumed the amino-form of these isomers and attempted to interpret the observed spectra. It will be expected that some contributions to the problem of the tautomerism of these molecules will be made also by such a study even if it is by an indirect method.

1) N. Mataga and K. Nishimonto, *Z. physik. Chem. N. F.*, **13**, 140 (1957).
2) N. Mataga, This Bulletin, **31**, 453 (1958).
3) N. Mataga, ibid., **31**, 459 (1958).
4) N. Mataga, ibid., **31**, 463 (1958).
5) N. Mataga, *Z. physik. Chem. N. F.*, **18**, 285 (1958).
6) See, for example, E. A. Steck and G. W. Ewing, *J. Am. Chem. Soc.*, **70**, 3397 (1948).
7) L. C. Anderson and N. V. Seeger, ibid., **71**, 340 (1949).
8) S. J. Angyal and C. L. Angyal, *J. Chem. Soc.*, **1952**, 1461.
9) T. Morita, presented at the "Symposium on the Electronic States of Molecules", held by Chem. Soc. Japan and Phys. Soc. Japan on october 13, 1958.
10) M. J. S. Dewar and L. Paoloni, *Trans. Faraday Soc.*, **53**, 261 (1957).

Method

Previously, Tsubomura[11] has studied the electronic spectra of substituted pyridines by the electron migration theory of Sklar and Herzfeld[12]. The general features of the substituted pyridine spectra have been well comprehended by his study. As pointed out by Goodman and Shull[13] in the case of substituted benzene spectra, however, for certain very strongly conjugating substituents, e. g., $-NH_2$, such a simplified perturbation method may be essentially invalid, and a more rigorous method will be needed. In the present study we have used the method developed by Longuet-Higgins and Murrell[14] for the study of the composite system. An excellent treatment based on an analogous idea has been developed independently by Nagakura and Tanaka[15]. Hereafter the outline of the method will be mentioned briefly.

Generally speaking, the electron transfer states are of two kinds, according as the electron is transferred from pyridine to the substituent or from the substituent to pyridine. In the present case, however, the substituent is a fairly strong electron donor and accordingly the configuration in which the electron is transferred from pyridine to the substituent will have a very high energy compared with the opposite case and may be neglected.

With this approximation, the problem is reduced to an evaluation of the interaction between the locally excited states of pyridine and one set of electron transfer states in which the electron is transferred from the substituent to pyridine.

If the SCFMO's of pyridine are written $\phi_1 \cdots\cdots \phi_p$ and those of the substituent $\theta_1 \cdots\cdots \theta_s$, then the energy of the electron transfer configuration $\chi_{s\to k}$ where one electron is transferred from an occupied orbital θ_s to an unoccupied orbital ϕ_k, is given by

$$E(\chi_{s\to k}) = \varepsilon_k - \varepsilon_s - \int \theta_s^2(i) \frac{e^2}{r_{ij}} \phi_k^2(j) \mathrm{d}v(i) \mathrm{d}v(j) \quad (1)$$

where ε_k and ε_s are SCFMO energies of ϕ_k and θ_s, respectively, and ϕ_k's are linear combinations of $2p\pi$ AO's $\phi_1 \cdots\cdots \phi_p$ of carbon or nitrogen

$$\phi_k = \sum_\mu c_{k\mu} \phi_\mu \quad (2)$$

Now, in actual computation, ε_s will be given, to a good approximation, by the ionization potential of ammonia. The difference of the observed[16] and calculated[17] values of electron affinity of benzene, $\Delta A = A_{\text{benz}}^{\text{obs}} - A_{\text{benz}}^{\text{calc}}$ has been added to the calculated values of ε_k's.

With neglect of differential overlap, the integral in 1 is reduced to

$$\sum_\mu \gamma_{s\mu} = \sum_\mu \int \theta_s^2(i) \frac{e^2}{r_{ij}} \phi_\mu^2(j) \mathrm{d}v(i) \mathrm{d}v(j) \quad (3)$$

These integrals have been replaced by the interaction energy of point charges centered on the substituent and on the μ atom, taking the length of bond joining the substituent and pyridine to be 1.46 Å. The matrix elements of the interaction between the various configurations have been evaluated from the following formulae,

$$(\chi_{s\to k} | \boldsymbol{H} | \chi_{j\to l}) = -\delta_{kl} \int \theta_s(i) H(i) \phi_j(i) \mathrm{d}v(i) \quad (4)$$

$$(\chi_{s\to k} | \boldsymbol{H} | \chi_0) = \sqrt{2} \int \theta_s(i) H(i) \phi_k(i) \mathrm{d}v(i) \quad (5)$$

$$(\chi_{s\to k} | \boldsymbol{H} | \chi_{s\to l}) = -(sk|G|sl) = -\int \theta_s^2(i) \frac{e^2}{r_{ij}} \phi_k(j) \phi_l(j) \mathrm{d}v(i) \mathrm{d}v(j) \quad (6)$$

The integral $\int \theta_s(i) H(i) \phi_j(i) \mathrm{d}v(i)$ can be reduced to $c_{jr} \int \theta_s(i) H(i) \phi_r(i) \mathrm{d}v(i)$ the substitutent being attached to carbon atom 'r'.

We have used a reasonable value for $\beta_{RS} = \int \theta_s(i) H(i) \phi_r(i) \mathrm{d}v(i) = -1.6$ eV. which is the same value as that used by Murrell[14] for the study of aniline. The wave functions and energies above the ground state of locally excited states of pyridine to be used in the present calculation are as follows[1]:

11) H. Tsubomura, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **78**, 293 (1957).
12) A. L. Sklar, *J. Chem. Phys.*, **7**, 987 (1939); K. F. Herzfeld, *Chem. Revs.*, **41**, 233 (1947); H. Baba and S. Nagakura, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **72**, 72 (1951).
13) L. Goodman and H. Shull, *J. Chem. Phys.*, **27**, 1388 (1957).
14) H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.*, **A68**, 601 (1955); J. N. Mureell, ibid., **68**, 969 (1955).
15) S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954); S. Nagakura, ibid., **23**, 1441 (1955); J. Tanaka, S. Nagakura and M. Kobayashi, ibid., **24**, 311 (1956); J. Tanaka and S. Nagakura, ibid., **24**, 1274 (1956).
16) Blackedge and Hush, quoted in N. S. Hush and J. A. Pople, *Trans. Faraday Soc.*, **51**, 600 (1955).
17) N. Mataga, K. Nishimoto and S. Mataga, This Bulletin, **32**, 395 (1959).

	E (eV.)
$\Psi(L_b) = 0.8202\chi_{3\to4} - 0.5720\chi_{2\to5}$	5.009
$\Psi(L_a) = 0.8688\chi_{3\to5} + 0.4951\chi_{2\to4}$	6.248
$\Psi(B_a) = 0.4951\chi_{3\to5} - 0.8688\chi_{2\to4}$	7.229
$\Psi(B_b) = 0.5720\chi_{3\to4} + 0.8202\chi_{2\to5}$	7.159

Results and Discussion

The interactions which occur between the various electronic states are shown in Table I.

As shown in Table I, in the case of 4-amino-pyridine, the seventh order matrix splits off into fourth and third order matrices, owing to the c_{2v} symmetry of the molecule.

Now, the wave functions and energies of the electronic states of 4-amino-pyridine are easily obtained as shown in Table II by solving the secular equations. In Table II, the corresponding quantities for aniline* are also indicated for the purpose of comparison.

TABLE I. THE MATRIX ELEMENTS OF THE INTERACTIONS BETWEEN THE ELECTRONIC STATES DUE TO THE CHARGE TRANSFER

2-Amino-pyridine

χ_0	L_b	L_a	B_a	B_b	$\chi_{s\to4}$	$\chi_{s\to5}$
0	0	0	0	0	−0.765	1.138
	5.009	0	0	0	0.652	0.166
		6.248	0	0	−0.144	0.691
			7.229	0	0.252	0.394
				7.159	0.455	−0.238
					5.554	0.696
						5.286

3-Amino-pyridine

χ_0	L_b	L_a	B_a	B_b	$\chi_{s\to4}$	$\chi_{s\to5}$
0	0	0	0	0	−0.617	−1.125
	5.009	0	0	0	0.660	−0.330
		6.248	0	0	0.286	0.699
			7.229	0	−0.502	0.398
				7.159	0.460	0.474
					5.593	−0.405
						5.313

4-Amino-pyridine

χ_0	L_a	B_a	$\chi_{s\to4}$	L_b	B_b	$\chi_{s\to5}$
0	0	0	1.333	5.009	0	−0.559
	6.248	0	0.484		7.159	0.802
		7.229	−0.850			6.221
			4.643			

TABLE II. THE WAVE FUNCTIONS AND ENERGIES OF THE ELECTRONIC STATES OF 4-AMINO-PYRIDINE AND ANILINE

4-Amino-pyridine

Energy (eV.)		χ_0	L_a	B_a	$\chi_{s\to4}$
−0.364	Ψ_0	0.963	0.019	−0.029	−0.263
4.609	$\Psi_{\mathrm{I}}(A_1)$	0.255	−0.261	0.286	0.885
6.352	$\Psi_{\mathrm{II}}(A_1)$	0.043	0.954	0.198	0.205
7.522	$\Psi_{\mathrm{III}}(A_1)$	0.057	0.122	−0.934	0.322
		L_b	B_b	$\chi_{s\to5}$	
4.750	$\Psi_{\mathrm{I}}(B_1)$	0.898	−0.138	0.416	
5.990	$\Psi_{\mathrm{II}}(B_1)$	0.425	0.511	−0.746	
7.651	$\Psi_{\mathrm{III}}(B_1)$	0.109	−0.846	−0.519	

Aniline

		χ_0	L_a	B_a	$\chi_{s\to4}$
−0.297	Ψ_0	0.972	−0.022	0.020	0.221
5.185	$\Psi_{\mathrm{I}}(A_1)$	0.192	0.550	−0.282	−0.762
6.404	$\Psi_{\mathrm{II}}(A_1)$	0.078	−0.793	−0.460	−0.384
7.315	$\Psi_{\mathrm{III}}(A_1)$	0.084	−0.250	0.839	−0.471
		L_b	B_b	$\chi_{s\to5}$	
4.704	$\Psi_{\mathrm{I}}(B_1)$	0.942	−0.092	0.316	
6.348	$\Psi_{\mathrm{II}}(B_1)$	0.296	0.702	−0.646	
7.588	$\Psi_{\mathrm{III}}(B_1)$	0.169	−0.704	−0.689	

As shown in Table II, in both 4-amino-pyridine and aniline, $\Psi_{\mathrm{I}}(B_1)$ is mainly contributed by L_b of pyridine and benzene, respectively, and accordingly the band due to the transition to this state may be regarded as a slightly modified L_b band in both of these molecules.

Contrary to this, $\Psi_{\mathrm{I}}(A_1)$ is mainly contributed by $\chi_{s\to4}$. Although the contribution of L_a to this state is still fairly great in the case of aniline, it becomes less prominent in the case of 4-amino-pyridine, and the contribution of $\chi_{s\to4}$ becomes more predominant (~80%). Therefore, the band due to the transition to this state in the case of 4-amino-pyridine may be called an intramolecular charge transfer band according to the naming of Nagakura and Tanaka[15].

Such a clear-cut classification of band character, however, does not hold in the case of the other isomers, various configurations being mixed in each state.

Now, whereas the MO ϕ_5 has the nodal plane through the C_2 axis of pyridine, the coefficient of AO at nitrogen has fairly great value in the MO ϕ_4. Accordingly, the increase of π-electron density or ring nitrogen caused by the substitution of an amino group for hydrogen may be determined by the degree of contribution of $\chi_{s\to4}$ to the ground state. This contribution is the greatest in the case of 4-amino-pyridine and the smallest in the case of

* The wave functions and energies of elctronic states of aniline collected in Table II are slightly different from those calculated by Murrell[14] because, in the present work, our parameters[1-5] have been used to calculate the wave functions and energies of benzene.

18) H. C. Longuet-Higgins, *J. Chem. Phys.*, **18**, 275 (1950).

TABLE III. THE WEIGHT (%) $\chi_{s\to4}$ IN THE GROUND STATE WAVE FUNCTIONS OF ISOMERIC AMINOPYRIDINES

	% weight of $\chi_{s\to4}$	pK_a at 20°C
4-Amino-pyridine	6.9	9.17
2-Amino-pyridine	2.3	6.86
3-Amino-pyridine	1.4	5.98

3-amino-pyridine as shown in Table III. This is in accordance with the conclusion obtained by the qualitative discussion of resonance theory. In addition, this is in good correspondence with the experimental pK_a values as indicated in Table III, if it is allowed to be assumed that pK_a is proportional to the π-electron density on ring nitrogen[18],**. In Table IV, the calculated and observed spectra are compared, where only the two bands which originate from the transitions to the lowest and second lowest excited states are shown, because of the lack of experimental values for the other states.

TABLE IV. CALCULATED AND OBSERVED SPECTRA OF ISOMERIC AMINO-PYRIDINES

Excitation energy (eV.)		Obsd. intensity[a] (ε_{max})
Calcd.	Obsd.[a]	
	2-Amino-pyridine	
4.865	4.20	4000
5.266	5.26	12000
	3-Amino-pyridine	
4.845	4.13	3000
5.137	5.18	10000
	4-Amino-pyridine	
5.114	~4.6	weak
4.973	5.1	14000

a) Ref. 6.

In Table IV, we have assigned the 5.114 eV. band of 4-amino-pyridine to the observed lowest energy band because, according to the calculated result, this band can be regarded as a slightly modified L_b band and consequently is likely to be weak. Contrary to this, the 4.973 eV. band is likely to be strong since it is the intramolecular charge transfer band. Accordingly we have assigned this band to the observed strong band at 5.1 eV.

It is evident from Table IV that the calculated two excitation energies in the case of 4-amino-pyridine are close to each other, while those in the case of the other isomers are more separated. This theoretical prediction is in qualitative or semiquantitative agreement with the experimental observation. Eventually, the general features of electronic spectra and structure of the isomeric amino-pyridines are well comprehended by the present calculation assuming the amino-form of these molecules.

Summary

The electronic spectra and structure of isomeric amino-pyridines have been studied theoretically employing the general method for the study of a composite system. The calculated results correspond satisfactorily with the experiment, in general, and the nature of electronic transitions in these molecules has been made clear. Thus it is evident that there is no difficulty in assuming the amino-form of these molecules in interpreting theoretically their electronic spectra and structure.

We are grateful to Dr. S. Nagakura of the University of Tokyo, Mr. T. Morita of Tokyo Metroporitan University and Mr. T. Kubota of Shionogi Co., Ltd. for their fruitful discussions.

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** Of course, this is no more than a limited and very approximate treatment as pointed out elesewhere[a].

a) S. Mataga and N. Mataga, *Z. physik. Chem. N. F.*, in press; S. Tsuno and N. Mataga, *Busseiron Kenkyu*, 3, Ser. 2, 665 (1958).

The Aconite Alkaloids. XXVIII.[1] *The Isolation of a New Alkaloid, Sachaconitine, from Aconitum Miyabei, Nakai*

By Harusada SUGINOME, Nobukatsu KATSUI and Gen HASEGAWA

(Received September 4, 1958)

In a previous paper of this series[2], it was reported that two alkaloids, miyaconitine, $C_{23}H_{29}O_6N$, and miyaconitinone, $C_{23}H_{27}O_6N$, had been isolated from the roots of Aconitum Miyabei, Nakai. The present paper describes the isolation and the characterization of a new alkaloid, sachaconitine, which was obtained, in addition to the above-mentioned alkaloids, from the same material.

In the isolation of miyaconitine and miyaconitinone[2], they were crystallized from fraction III[3] and their mother liquors still contained appreciable amounts of basic substances.

The amorphous base obtained from the mother liquors was dissolved in 1 N-acetic acid and 10 % aqueous sodium carbonate was added to the solution. The precipitate was filtered off, and the filtrate was extracted with ether. The extracted base was then converted into the perchlorate. The crystalline perchlorate is easily soluble in alcohol and in hot water. From alcohol it crystallized in needles, m. p. 188~189°C, $[\alpha]_D$ −23.72° and from water its trihydrate crystallized in prisms, m. p. 180~185°C after softening at 100°C.

The composition, $C_{23}H_{37}O_4N \cdot HClO_4$, compares favorably with the analytical results; the formula was ascertained by analyses of acid oxalate, m. p. 182~183°C, aurichloride, m. p. 198~199°C, free base, m. p. 129~130°C, $[\alpha]_D$ −13.08°, and the diacetyl derivative, m. p. 114~116°C, $[\alpha]_D$ −10.87°.

It appears that this alkaloid has not yet been described, and the name "sachaconitine" was given to the new alkaloid. The analyses do not discriminate between H_{37} and H_{39} in the composition. Though the analytical result of diacetyl sachaconitine favors the latter, the formula with H_{37} seems more probable since it brings sachaconitine into line with other aconite alkaloids for reasons described below.

The base is stable against alkali and acid and thus contains no ester group. Acetylation of the base with acetyl chloride yielded a diacetyl compound which gave the original base on saponification. The presence of two methoxyl groups was confirmed by the Micro-Zeizel methoxyl determination. Hence the base contains two hydroxyl and two methoxyl groups.

The base gave ethyl iodide in the Herzig-Mayer *N*-alkyl determination and acetaldehyde on oxidation with permanganate, similarly to other aconite alkaloids containing an *N*-ethyl group, for example, lycoctonine[4-6], delpheline[7], and aconitine[8]. Coockson and Trevett[7] and Abubakirov and Yunusov[9] succeeded in confirming the presence of a simple *N*-alkyl group by converting de-ethyl derivatives (nor-componds) into the corresponding alkaloids. It appears, therefore, that the new alkaloid also contains a simple *N*-ethyl group.

On the other hand, it has been reported[10] that atisine with an oxazolidine ring[11] gave also ethyl iodide in the *N*-alkyl determination by the same method. But sachaconitine contains two methoxyl and two hydroxyl groups, and no more oxygen atoms to make such a ring.

The base was not hydrogenated with platinum oxide in acidic solution. The ultraviolet spectrum of the base showed only end absorption (Fig. 1) quite similarly

1) Part XXVII, S. Furusawa, This Bulletin, **32**, 399 (1959).

2) H. Suginome, S. Furusawa, Y. Chiba and S. Kakimoto, *J. Fac. Sci., Hokkaido Univ., Ser. III. Chem.*, **4**, 1 (1950).

3) Fraction I is the part readily precipitable with aqueous ammonia. The mother liquor from fraction I is shaken with chloroform and then the resulting chloroform extract is treated with 1N-hydrochloric acid. Then the material obtained from chloroform solution is called fraction II and the part precipitated with ammonia from the acidic solution is called fraction III.

4) H. Suginome and K. Ohno, *J. Fac. Sci., Hokkaido Univ., Ser. III. Chem.*, **4**, 36 (1950).

5) M. S. Rabinovich and R. A. Konovalova, *J. Gen. Chem. (U. S. S. R.)*, **19**, 1387 (1949).

6) J. A. Goodson, *J. Chem. Soc.*, **1945**, 145.

7) R. C. Cookson and M. E. Trevett, ibid., **1956**, 2689.

8) R. Majima and K. Tamura, *Ann.*, **526**, 116 (1936).

9) N. K. Abubakirov and S. Yu. Yunusov, *J. Gen. Chem. U. S. S. R.* **27**, 733 (1954).

9) C. F. Huebner and W. A. Jacobs, *J. Biol. Chem.*, **170**, 515 (1947); **174**, 1001 (1948).

11) S. W. Pelletier and W. A. Jacobs, *J. Am. Chem. Soc.*, **76**, 4496 (1954).

to lycoctonine[12] possessing no unsaturation.

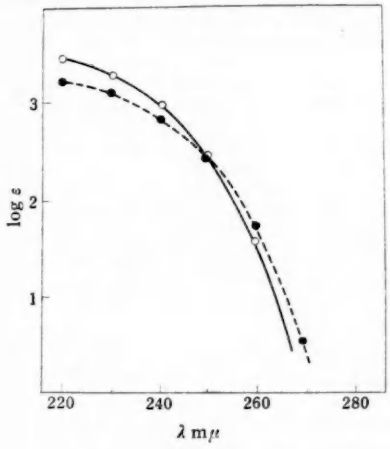

Fig. 1
Sachaconitine —○—○—
Lycoctonine ---●---●---

The above results relate the formula $C_{23}H_{37}O_4N$ of sachaconitine to other aconite alkaloids possessing the $C_{19}H_{29}N$ skeleton which is believed to be the fundamental base as pointed out by Suginome and Ohno[4], by Stern[13] and by Edwards and Marion[12]. Accordingly the formula can be extended as follows:

$$C_{19}H_{24}\begin{cases}(OCH_3)_2\\(OH)_2\\N{-}C_2H_5\end{cases}$$

The three alkaloids, miyaconitine, miyaconitinone and sachaconitine, were thus isolated from fraction III; they had no toxicity. In general, toxic bases containing an acyl and an aroyl group in aconite roots have been obtained from fraction I[3].

In attempts to isolate a crystalline substance from the amorphous base from the same roots, the fourth alkaloid, $C_{33}H_{45}O_8N$, m. p. 167~168°C, $[\alpha]_D$ +20.1° was isolated from fraction I. It agrees with delphinine in the composition but not in physical constants. Thus the name "base D" was assigned tentatively to this alkaloid. The investigation concerning the identification of "base D" with delphinine will be reported in a later paper.

12) O. E. Edwards and Leo Marion, *Can. J. Chem.*, **30**, 627 (1952).
13) E. S. Stern, "The Aconitum and Delphinium Alkaloids" in "The Alkaloids", Vol. IV, edited by R. H. F. Manske and H. L. Holmes, Academic Press Inc., New York (1954), p. 275.

Experimental

Isolation of Sachaconitine Perchlorate.— The residue of evaporation of the mother liquors from crystallization of miyaconitine and miyaconitinone perchlorate was converted into the free base by the usual method of treatment with chloroform and alkali. Amorphous basic material (14 g.) thus obtained was neutralized with 10% acetic acid and diluted with water. To the diluted solution 30% aqueous sodium carbonate was added until no more precipitate was produced. The precipitate was filtered off, but not examined.

The filtrate was subjected to continuous extraction with ether. Miyaconitinone remaining in the crude material separated out in prisms in 1 hr. Without removing it, extraction was continued further for 40 hr.

The extract, after being separated from miyaconitinone and dried over anhydrous sodium sulfate, was evaporated under reduced pressure to yield 7.5 g. of an amorphous material. This material was again neutralized with 0.1 N-hydrochloric acid and to the resulting solution 30% aqueous sodium perchlorate was added in small portions. On addition of the perchlorate the solution first became turbid but soon turned clear on stirring with further portions of the perchlorate solution. When turbidity was no longer noticed, the resulting solution was warmed on a steam bath until it became clear, treated with charcoal and filtered while hot. The perchlorate of the base separated as an oil on cooling the solution. The aqueous layer was decanted off and the oil was allowed to stand at room temperature overnight to give a gum containing some crystals which could not be separated. The gum was dissolved in a small amount of methanol and the solution was diluted with water until faint cloudiness remained. Concentration of the solution at room temperature gave 5 g. of crude sachaconitine perchlorate.

Sachaconitine perchlorate is easily soluble in alcohol and in hot water, and slightly soluble in cold water. From alcohol it crystallized in needles, m. p. 188~189°C, $[\alpha]_D^{20}$ −23.72° (C, 1.79 in alc.), and from water the trihydrate crystallized in plates, m. p. 188~189°C after softening at 100°C. The trihydrate gave the same m. p. and $[\alpha]_D$ after being dried over P_2O_5 under reduced pressure.

Anal. Found (anhydrous): C, 56.06; H, 7.70; N, 2.47; Cl, 7.34. Calcd. for $C_{23}H_{37}O_4N\cdot HClO_4$: C, 56.09; H, 7.72; N, 2.84; Cl, 7.21. Calcd. for $C_{23}H_{39}O_4N\cdot HClO_4$: C, 55.91; H, 8.16; N, 2.84; Cl, 7.18. Found (trihydrate): H_2O, 9.88. Calcd. for $C_{23}H_{37}O_4N\cdot HClO_4\cdot 3H_2O$: H_2O, 9.89%.

Sachatonitine.— The solution of the perchlorate in water was warmed to 50~60°C, and basified with aqueous sodium carbonate. The free base separated out as a resin, which soon solidified on cooling. Colorless plates from alcohol, m. p. 129~130°C, $[\alpha]_D^{20}$ −13.08° (C, 2.35 in 95% alc.).

Anal. Found: C, 70.35; H, 9.39; N, 3.59%. Calcd. for $C_{23}H_{37}O_4N$: C, 70.58; H, 9.46; N, 3.55%. Calcd. for $C_{25}H_{39}O_4N$: C, 70.19; H, 9.99; N, 3.56%.

The ultraviolet spectrum of the base showed only end absorption (Fig. 1).

The base was subjected to the Micro-Zeizel methoxyl, and the Herzig-Meyer *N*-alkyl determinations.

Anal. Found: CH_3O-, 15.91; C_2H_5-, 7.02. Calcd. for $C_{19}H_{26}O_2(OCH_3)_2 \cdot N \cdot C_2H_5$: CH_3O-, 15.85; C_2H_5-, 7.42%. Calcd. for $C_{19}H_{28}O_2(OCH_3)_2 \cdot N \cdot C_2H_5$: CH_3O-, 15.77; C_2H_5-, 7.38%.

The base (100 mg.) was submitted to the conventional Herzig-Meyer *N*-alkyl determination; the gases which evolved during pyrolysis of the hydroiodide were passed into a cold solution of trimethylamine in alcohol. The ethanol-soluble salt, ethyltrimethyl-ammonium iodide, was obtained from the trimethylamine solution.

Anal. Found: I, 59.27. Calcd. for $C_5H_{14}NI$: I, 59.04%.

The base absorbed no hydrogen in the presence of PtO_2 in acetic acid solution.

A solution of sachaconitine in 1N-potassium hydroxide in 50% aqueous methanol was refluxed on a steam bath for 30 min. From the resulting reaction mixture no acidic substance was detected, but unchanged sachaconitine was recovered.

Estimation of Acetaldehyde.—To a cold solution of 400 mg. of sachaconitine in 3 cc. of 1N-sulfuric acid, 15 cc. of 2% aqueous potassium permanganate was added dropwise in the course of 3 hr. After standing overnight, the manganese dioxide was filtered off and washed twice with water. The combined filtrate and washings were distilled into a receiver containing 50 cc. of a slightly alkaline solution of 280 mg. of dimedone. Acidification with hydrochloric acid gave 73 mg. of acetaldehyde-dimedone, m. p. 139~140°C. It showed no depression of the melting point on admixture with an authentic specimen.

Sachaconitine Aurichloride.—The compound, prepared from the base and auric chloride, crystallized from a mixture of acetone and ether in prisms, m. p. 197~198°C (decomp.).

Anal. Found: Au, 26.88. Calcd. for $C_{23}H_{37}O_4N \cdot AuCl_3 \cdot HCl$: Au, 26.96%. Calcd. for $C_{23}H_{39}O_4N \cdot AuCl_3 \cdot HCl$: Au, 26.88%.

Sachaconitine Acid Oxalate.—The compound, prepared from the base and oxalic acid, crystallized from absolute alcohol in needles, m. p. 182~183°C, $[\alpha]_D^{20}$ −29.71° (C, 0.69 in 70% alc.)

Anal. Found: C, 61.70; H, 8.16. Calcd. for $C_{23}H_{37}O_4N \cdot C_2H_2O_4$: C, 62.35; H, 8.16. Calcd. for $C_{23}H_{39}O_4N \cdot C_2H_2O_4$: C, 62.09; H, 8.55%.

Sachaconitine Hydrochloride.—Dried hydrogen chloride was passed into a solution of the base in anhydrous acetone to produce a white precipitate. Reprecipitation by adding acetone to a very concentrated alcoholic solution of the precipitate gave sachaconitine hydrochloride in colorless needles, m. p. 203~204°C, $[\alpha]_D^{20}$ −30.43° (C, 0.78 in 95% alc.). No satisfactory analytical data have been found because of the extremely hygroscopic property of this compound.

Diacetylsachaconitine.—The base (1 g.) was treated with 4 g. of acetyl chloride in a sealed tube at room temperature for 5 days. The excess of the reagent was distilled off under reduced pressure and water was added. The aqueous solution was basified and extracted with chloroform. The residual product, obtained by evaporation of the chloroform, was crystallized from aqueous alcohol to give 400 mg. of plates, m. p. 114~116°C, $[\alpha]_D^{20}$ −10.87° (C, 1.70 in 95% alc.).

Anal. Found: C, 68.03, H, 8.92, N, 3.12. Calcd. for $C_{22}H_{35}O_2N \cdot (OCOCH_3)_2$: C, 68.18; H, 8.69; N, 2.95%. Calcd. for $C_{23}H_{37}O_2N \cdot (OCOCH_3)_2$: C, 67.89; H, 9.07; N, 2.93%.

On saponifying diacetylsachaconitine with alkali sachaconitine was regenerated.

Isolation of "Base D".—Fraction 1[3] (10 g.) was refluxed with 100 cc. of ether for 30 min. on a steam bath and the ether insoluble residue was again refluxed with 50 cc. of fresh ether. Complete removal of the solvent from the combined extracts gave 8 g. of amorphous yellow powder, which was neutralized with 1N-acetic acid and diluted to 100 cc. with water. To the resulting solution powdered sodium bicarbonate was added in small portions until no further precipitation was noticed. After being left to stand for 30 min., the resinous precipitate (Ia) was filtered off. From the filtrate a precipitate (Ib) was obtained on adding 50 cc. of 20% aqueous sodium carbonate, and another (Ic) on adding ammonia. No crystallizable alkaloids were obtaind from Ia and Ic. The fractional precipitation of Ib with sodium bicarbonate and carbonate was repeated twice; then 5 g. of powder precipitating with sodium carbonate was obtained. This material was dissolved in alcohol and the solvent was allowed to evaporate at room temperature, because heating of the solution caused crystallization with difficulty. Thus 2.5 g. of the crystalline "base D" was deposited from the alcoholic solution.

"Base D" is readily soluble in alcohol, chloroform and ether and insoluble in petroleum ether. It was recrystallized from a mixture of ether and petroleum ether in needles, m. p. 167~168°C, $[\alpha]_D^{20}$ +20.10° (C, 2.05 in 95% alc.).

Anal. Found: C, 66.13; H, 7.54; N, 2.23. Calcd. for $C_{33}H_{45}O_9N$: C, 66.09; H, 7.56; N, 2.34%.

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Studies on Copper Phthalocyanine and its Chlorinated Derivatives Based upon the X-ray Diffraction Patterns

By Masahiro SHIGEMITSU

(Received August 13, 1958)

The molecular structure of copper phthalocyanine was first investigated by R. P. Linstead et al.[1] and later J. M. Robertson[2] studied its crystal structure by means of X-ray diffraction. He had only one form of copper phthalocyanine —namely, the α-form. This was prepared by sublimation as large needle crystal unsuited for pigment use. In order to reduce the particle size of copper phthalocyanine, the needle pigment is dissolved in concentrated sulfuric acid, and then is precipitated in fine particles by adding the acid solution to a large quantity of water with agitation. The first commercial pigment is the fine particles thus obtained. G. von Susich[3] showed that copper phthalocyanine conditioned in the above manner had a different X-ray diffraction pattern from that of the sublimed product studied by J. M. Robertson. Here the J. M. Robertson form is called α-form, because historically this crystal form was the first to be identified, and the first commercial pigment form is called β-form.

The copper phthalocyanine and lowly chlorinated copper phthalocyanines (containing chlorine atoms not more than six) are mostly used in blue pigments, while the highly chlorinated copper phthalocyanines (containing about 14 chlorine atoms) in green pigments. As to polymorphism of chlorinated copper phthalocyanines, D. N. Kendall[4], on the basis of infrared absorption measurement, reported that there were also two forms of crystal structures, α- and β-forms, in copper monochlorophthalocyanine (no mention is made of position of chlorine atom), whereas only one form of crystal structure was identified in highly chlorinated copper phthalocyanine green.

The author worked out X-ray diffraction patterns on twelve samples, six in needle forms and six in granular ones, of the following compounds; copper phthalocyanine, copper tetra-(3)-chlorophthalocyanine, copper tetra-(4)-chlorophthalocyanine, copper octa-(3, 6)-chlorophthalocyanine, copper octa-(4, 5)-chlorophthalocyanine and copper hexadecachlorophthalocyanine; the polymorphism was hereby investigated with copper phthalocyanine and its chlorinated derivatives.

Experimental

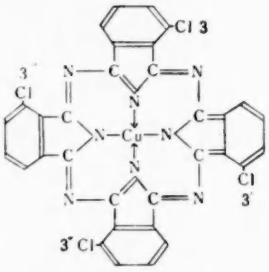
Materials.—Two forms of crystals, needle and granular forms, of copper phthalocyanine derivatives of different chlorine contents were synthesized as follows.

(1) *α-Form (I) and β-form (II) copper phthalocyanines.*—Synthesis of copper phthalocyanine was carried out following the method described in Ref. 5. From the product, then, α- and β-form crystals were obtained by the following procedure. First, copper phthalocyanine was put into a quartz glass tube, heated up to 550~580 C in an electric furnace, making the needle crystal of I sublime. α-Form crystal thus obtained was dissolved in 98% sulfuric acid of 20 times in weight at room temperature and allowed to stand 4 hr. Then, poured into ice water, granular II was formed, and separated through filtration. By chlorine analysis, it was found that there was just a trace of chlorine content, that is, 0.11%. Micro-Carius method was applied in all the following chlorine analyses.

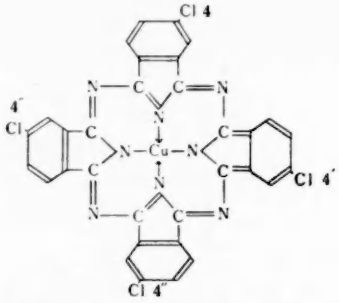
Granular I of a size which seemed to be suitable for pigment was prepared by the method described in Ref. 6. Namely, 100 cc. of acetone, 1.2 kg. of steel shots of approximately 3 mm. in diameter and 5 g. of I in needle form which was obtained by sublimation were put into a porcelain pot of 500 cc. capacity and pulverized at 100 r. p. m. for 72 hr.; the product was granular I in brilliant greenish blue.

(2) *Copper tetra-(3)-chlorophthalocyanine (III) and copper tetra-(4)-chlorophthalocyanine (IV).*—

1) R. P. Linstead et al., *J. Chem. Soc.*, **1934**, 1036.
2) J. M. Robertson, ibid., **1935**, 615; ibid., **1936**, 1195; ibid., **1937**, 219.
3) G. von Susich, *Anal. Chem.*, **22**, 425 (1950).
4) D. N. Kendall, ibid., **25**, 382 (1953).
5) M. Shigemitsu, *J. Chem. Soc, Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **62**, 110 (1959) (presented at the 10th Annual Meeting of the Chemical Society of Japan held in April, 1957).
6) U. S. Pat. 2,556,726 (1951); U. S. Pat. 2,556,727 (1951); U. S. Pat. 2,556,728 (1951); U. S. Pat. 2,556,730 (1951).
7) M. Shigemitsu, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **62**, 112 (1959) (presented at the Autumnal Joint Meeting of Chemical Society of Japan with other Societies, Tokyo, 1957).

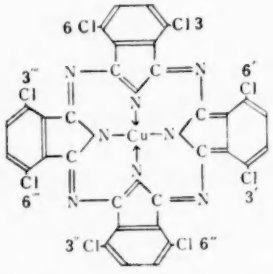


Copper tetra-(3)-chlorophthalocyanine

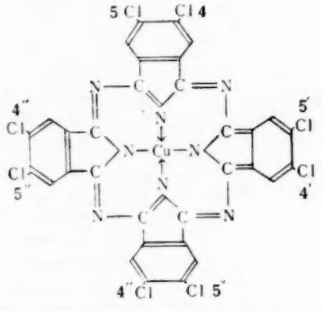


Copper tetra-(4)-chlorophthalocyanine

Fig. 1



Copper octa-(3, 6)-chlorophthalocyanine



Copper octa-(4, 5)-chlorophthalocyanine

Fig. 2

III and IV were prepared by condensing 3- and 4-monochlorophthalic anhydrides (see below) respectively with urea and copper in trichlorobenzene. From the mixture of monochlorophthalic anhydrides prepared following the method in Ref. 7, separated 3-monochlorophthalic anhydride, m. p. 121～122°C (reported m. p. 122°C)[8] (*Anal.* Found: Cl, 19.40%) and 4-monochlorophthalic anhydride, m. p. 97～98°C (reported m. p. 98°C[8]) (*Anal.* Found: Cl, 19.44%) by repeating recrystallization with toluene-ethanol (1 : 1) solvent. The chlorine contents in III and IV derived from these 3- and 4-monochlorophthalic anhydrides were 19.72% and 19.80%, respectively.

Both of III and IV prepared in this way were of needle crystals. To convert them into granular forms, they were dissolved in 98% sulfuric acid of 20 times in weight at room temperature, allowed to stand for 4 hr. and poured into ice water.

Since chlorinated copper phthalocyanines do not sublime, it is impossible to obtain the needle crystals by sublimation, but they can be obtained by condensing various chlorophthalic anhydrides together with urea and copper in trichlorobenzene. Therefore, this method was adapted later in obtaining the needle crystals of various chlorinated copper phthalocyanines.

8) V. Villiger, *Ber.*, **42**, 3532 (1909).

(3) *Copper octa-(3, 6)-chlorophthalocyanine (V) and copper octa-(4, 5)-chlorophthalocyanine (VI).* —V which was synthesized following the method described in Ref. 7 was taken up; it showed a chlorine content of 33.21% and was of needle crystal.

VI was synthesized by condensing 4, 5-dichloro phthalic anhydride (see below) together with urea and copper in trichlorobenzene; it showed a chlorine content of 33.23% and was of needle crystal. 4, 5-Dichlorophthalic anhydride, m. p. 185～186.5°C (reported m. p. 185～187°C)[9] (*Anal.* Found: Cl, 32.60%) was separated from the mixture of dichlorophthalic anhydrides[7] with toluene-ethanol (1:1) solvent.

To convert them into granular forms, they were dissolved in chlorosulfonic acid of 20 times in weight at room temperature, allowed to stand 4 hr. and poured into ice water.

(4) *Copper hexadecachlorophthalocyanine (VII).* —Needle-formed VII synthesized following the method described in Ref. 7, with chlorine content of 50.33%, was used. Granular VII was prepared by dissolving needle-formed VII in chlorosulfonic acid of 30 times in weight at room temperature, allowing it to stand for 4 hr. and then pouring it into ice water.

Methods.—(1) *Observation of pigment forms.* —Two types of samples were prepared as follows. One was made first by washing with water the

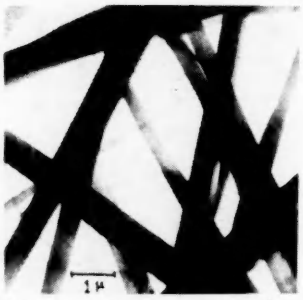


Fig. 3. α-Form copper phthalocyanine (I) (needle form)

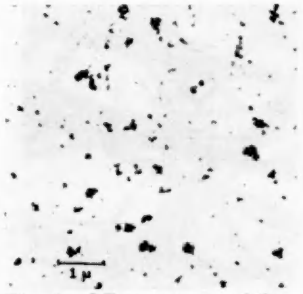


Fig. 4. β-Form copper phthalocyanine (II) (granular form)

Fig. 5. Copper tetra-(3)-chlorophthalocyanine (III) (needle form)

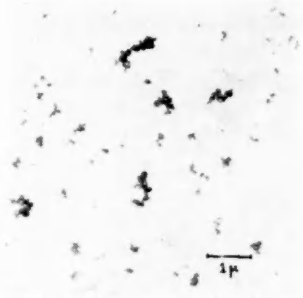


Fig. 6. Copper tetra-(3)-chlorophthalocyanine (III) (granular form)

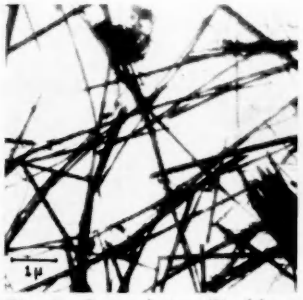


Fig. 7. Copper tetra-(3)-chlorophthalocyanine (III) (boiled for 10 hr. in trichlorobenzene)

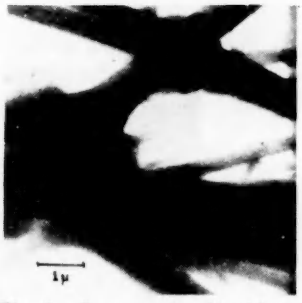


Fig. 8. Copper tetra-(4)-chlorophthalocyanine (IV) (needle form)

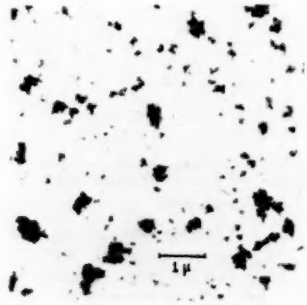


Fig. 9. Copper tetra-(4)-chlorophthalocyanine (IV) (granular form)

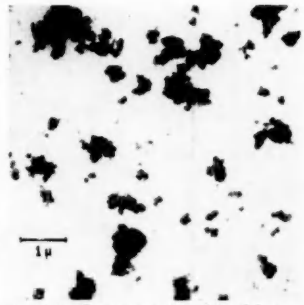


Fig. 10. Copper tetra-(4)-chlorophthalocyanine (IV) (boiled for 10 hr. in trichlorobenzene)

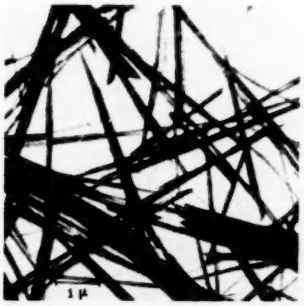


Fig. 11. Copper octa-(3,6)-chlorophthalocyanine (V) (needle form)

granular pigments reprecipitated from the solution in 98% sulfuric acid of chlorosulfonic acid, and then placing and drying a drop of pigment suspension in water upon the collodion film of sample holder. The other was prepared first by drying the pigments obtained in any way other than by reprecipitation and then by sprinkling them over the collodion film of sample holder. The author photographed them with an electron microscope (Hitachi Works) at 2,000 direct magnification. The pictures were enlarged again by 10,000 times, and by means of these enlargements, their forms were closely examined.

(2) ***Changes in pigment shade accompanied by being heated in trichlorobenzene.***—Granular pigments prepared by reprecipitation were heated in the boiling trichlorobenzene (b. p. 200~210°C) of 100 times in weight for 10 hr, and then filtered. After the sticking trichlorobenzene was eliminated by washing with ethanol, they were

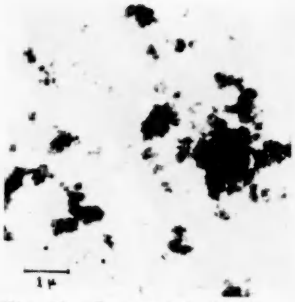


Fig. 12. Copper octa-(3,6)-chlorophthalocyanine (V) (granular form)

Fig. 13. Copper octa-(4,5)-chlorophthalocyanine (VI) (needle form)

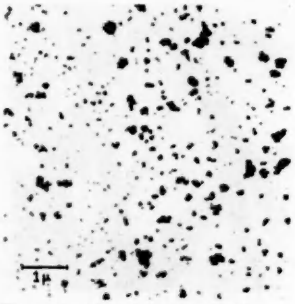


Fig. 14. Copper octa-(4,5)-chlorophthalocyanine (VI) (granular form)

Fig. 15. Copper hexadecachlorophthalocyanine (VII) (needle form)

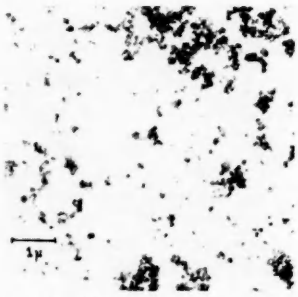


Fig. 16. Copper hexadecachlorophthalocyanine (VII) (granular form)

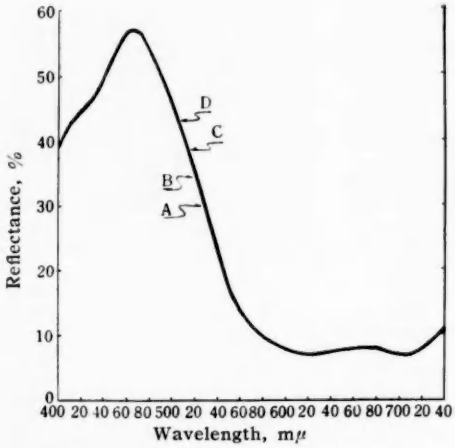


Fig. 17. α-Form copper phthalocyanine (I), (granular form):
A, untreated; B, stood for 5 days;
C, boiled for 1 hr.; D, boiled for 10 hr.

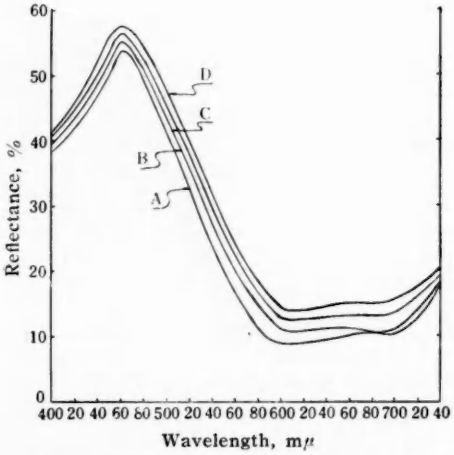


Fig. 18. β-Form copper phthalocyanine (II), (granular form):
A, untreated; B, stood for 5 days;
C, boiled for 1 hr.; D, boiled for 10 hr.

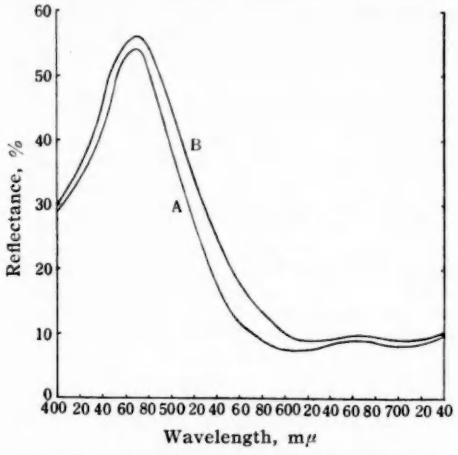


Fig. 19. Copper tetra-(3)-chlorophthalocyanine (III), (granular form):
A, untreated; B, boiled for 10 hr.

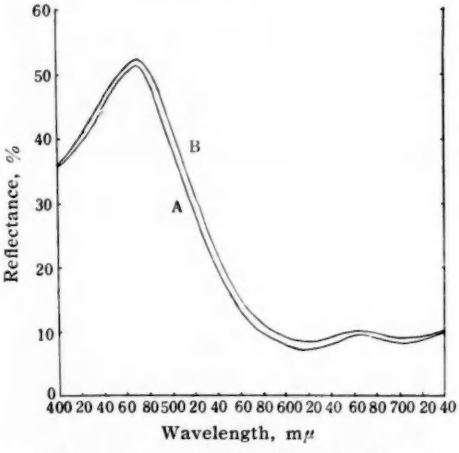


Fig. 20. Copper tetra-(4)-chlorophthalocyanine (IV), (graunlar form):
A, untreated; B, boiled for 10 hr.

dried at about 60°C. The pigments thus obtained and the original untreated ones were mixed respectively with polymerized linseed oil of 1.5 times in weight and were made into paste by grinding 400 rounds in a Hoover automatic muller. To 1 part of each paste was added 70 parts of zinc white paste (obtained by grinding 2 parts of zinc oxide with 1.5 parts of polymerized linseed oil), which was applied 0.5 mm. in thickness on a coated paper with a bladeoapplicator (Gardner Laboratory). These were dried at room temperature, their reflectance curves were obtained with a recording spectrophotometer (General Electric Co.), and calculation was thereby conducted.

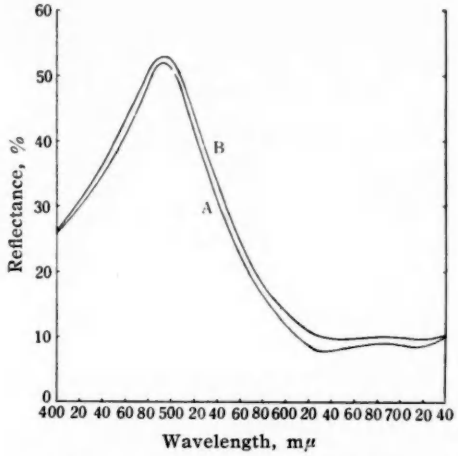


Fig. 21. Copper octa-(3,6)-chlorophthalocyanine (V), (granular form):
A, untreated; B, boiled for 10 hr.

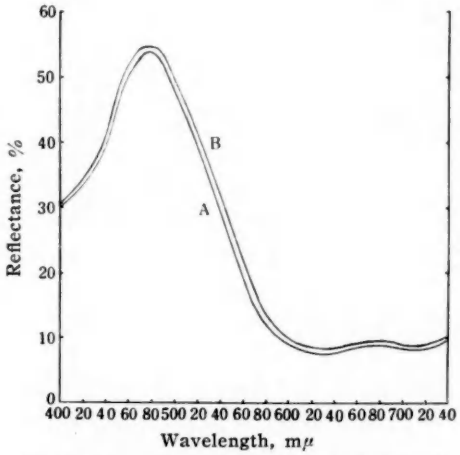


Fig. 22. Copper octa-(4,5)-chlorophthalocyanine (VI), (granular form):
A, untreated; B, boiled for 10 hr.

(3) *Crystal structures of pigments.*—The X-ray diffraction patterns of each pigment were obtained with a recording X-ray diffraction apparatus (Philips Co.).

Results. — (1) *Forms of pigments.* — Photos taken with an electron microscope are shown (Fig. 3 to Fig. 16). Fig. 3 shows I obtained by sublimation, while Figs. 5, 8, 11, 13 and 15 show chlorinated copper phthalocyanines obtained by synthesis in trichlorobenzene; they are all in needle forms. Figs. 4, 6, 9, 12, 14 and 16 show II and chlorinated copper phthalocyanines, all in granular forms, obtained by dissolving the needle crystals in 98% sulfuric acid or chlorosulfonic

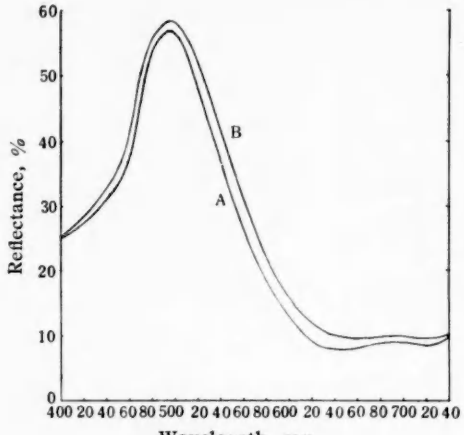


Fig. 23. Copper hexadecachlorophthalocyanine (VII), (granular form):
A, untreated; B, boiled for 10 hr.

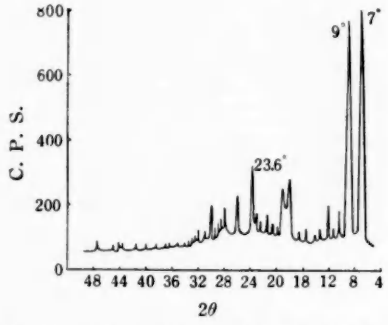


Fig. 24. α-Form copper phthalocyanine (I), (needle form)

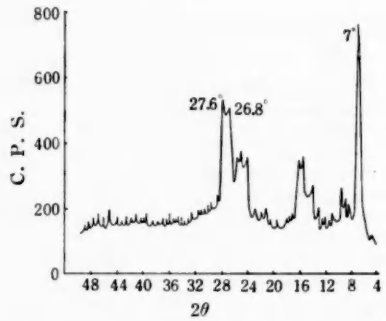


Fig. 25. β-Form copper phthalocyanine (II), (graunlar form)

acid and pouring them into ice water.

Fig. 7 shows the needle crystal prepared by boiling the granular III (Fig. 6) in trichlorobenzene for 10 hr. This change resembles the transformation of granular II into needle-formed I, which appears when the former is heated in organic solvents[9,10]. However, no change can be detected in case IV (Fig. 9) when it is heated in the boiling trichlorobenzene for 10 hr, as is manifested from Fig. 10.

It is known that, when a small amount of chlorine is introduced by the direct chlorination of copper phthalocyanine, a compound can be obtained which does not show any crystal growth in organic solvents[11]. In this case, chlorine is first substituted at the 4- or 5-position of phthalocyanine nucleus[7,12]. Meanwhile, according to Bansho et al.[13], no crystal growth takes place in the case of chlorinated copper phthalocyanine obtained from the direct chlorination or 4-monochlorophthalic anhydride. These facts are in good harmony with the results by the author.

As to copper octachlorophthalocyanines, on the other hand, no difference is formed any more in the crystal growth; independently of the positions which are occupied by chlorine atoms, 3,6- or 4,5-positions of phthalocyanine nucleus, no crystal growth takes place even in case copper octachlorophthalocyanines are boiled in trichlorobenzene for 10 hr. The case of granular VII is also quite the same.

(2) *Changes in pigment shade.* — Reflectance curves obtained with a recording spectrophotometer are shown (Fig. 17 to Fig. 23). Table I gives the data of these curves expressed in terms of C. I. E. Notation. In this table, *Y* denotes luminosity, *Pe* purity and λ_D dominant wavelength.

It is evident from Fig. 17, that granular I, even though boiled in trichlorobenzene for 10 hr.,

TABLE I. C. I. E. NOTATION

Sample	Reflectance curve	*Y* %	*Pe* %	λ_D mμ
A	Fig. 17	20.7	56.0	480.7
B		20.7	56.0	480.7
C		20.7	56.0	480.7
D		20.7	56.0	480.7
A	Fig. 18	19.1	55.0	475.8
B		23.4	52.0	478.8
C		24.2	51.0	479.7
D		25.2	49.6	479.8
A	Fig. 19	19.7	58.4	481.5
B		21.6	54.2	484.2
A	Fig. 20	18.4	56.1	478.3
B		18.5	56.0	478.7
A	Fig. 21	25.2	49.6	485.0
B		25.5	48.8	485.9
A	Fig. 22	21.6	55.8	482.5
B		21.9	55.6	482.7
A	Fig. 23	30.3	36.8	492.6
B		31.2	35.7	494.5

9) FIAT Report, No. 1313, **3**, 446 (1948).
10) U. S. Pat. 2,486,351 (1949).
11) U. S. Pat. 2,615,026 (1952); U. S. Pat. 2,618,642 (1952).
12) R. P. Linstead et al., *J. Chem. Soc.*, **1939**, 1820.
13) Y. Bansho et al., *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **59**, 67 (1956).

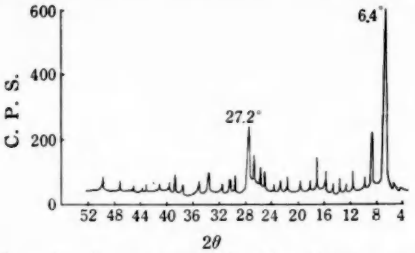


Fig. 26. Copper tetra-(3)-chlorophthalocyanine (III), (needle form)

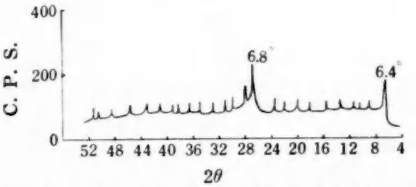


Fig. 27. Copper tetra-(3)-chlorophthalocyanine (III), (granular form)

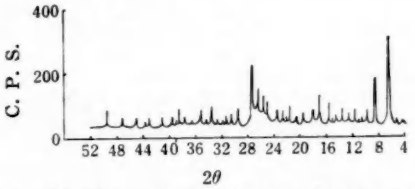


Fig. 28. Copper tetra-(3)-chlorophthalocyanine (III), (granular form); boiled for 10 hr.

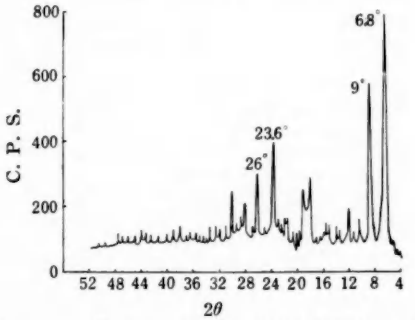


Fig. 29. Copper tetra-(4)-chlorophthalocyanine (IV), (needle form)

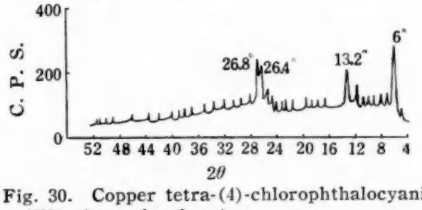


Fig. 30. Copper tetra-(4)-chlorophthalocyanine (IV), (granular form)

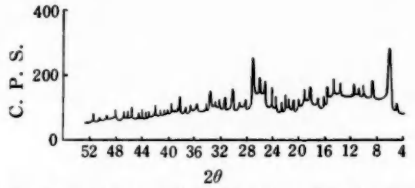


Fig. 31. Copper tetra-(4)-chlorophthalocyanine (IV), (granular form); boiled for 10 hr.

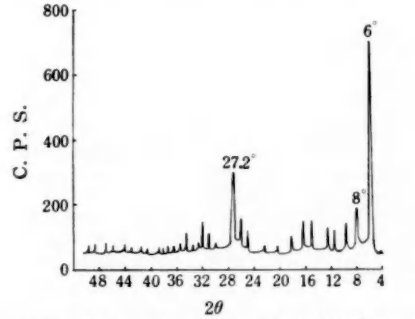


Fig. 32. Copper octa-(3, 6)-chlorophthalocyanine (V), (needle form)

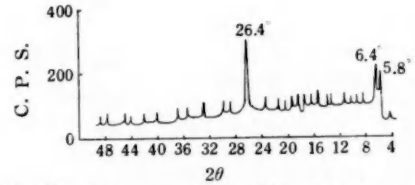


Fig. 33. Copper octa-(3, 6)-chlorophthalocyanine (V), (granular form)

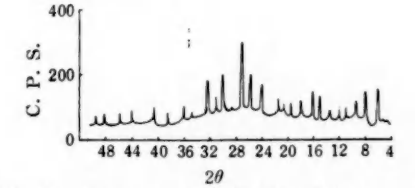


Fig. 34. Copper octa-(3, 6)-chlorophthalocyanine (V), (granular form); boiled for 10 hr.

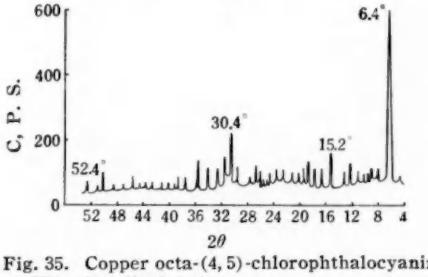


Fig. 35. Copper octa-(4, 5)-chlorophthalocyanine (VI), (needle form)

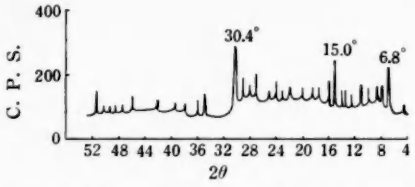


Fig. 36. Copper octa-(4, 5)-chlorophthalocyanine (VI), (granular form)

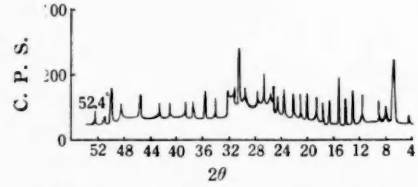


Fig. 37. Copper octa-(4, 5)-chlorophthalocyanine (VI), (granular form); boiled for 10 hr.

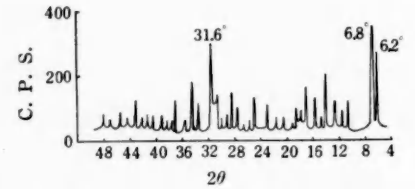


Fig. 38. Copper hexadecachlorophthalocyanine (VII), (needle form)

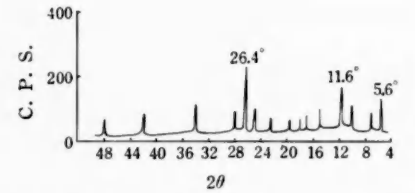


Fig. 39. Copper hexadecachlorophthalocyanine (VII), (granular form)

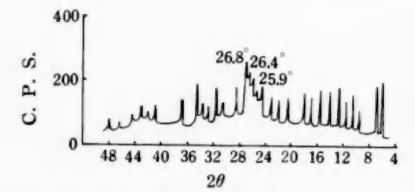


Fig. 40. Copper hexadecachlorophthalocyanine (VII), (granular form); boiled for 10 hr.

causes neither crystal growth nor color change, while in the case of granular II the crystal grows with remarkable change of shade, as shown in Fig. 18. As to the shade, its dominant wavelength shifts to the longer wavelength side by 4 mμ, that is, yellowishness increases.

Granular III grows into needle crystal and, as is clear from Fig. 19, changes in its shade. With a shift of its dominant wavelength by 2.7 mμ, it increases in yellowishness. On the contrary, its isomer, granular IV causes no crystal growth and scarcely changes at all in its shade, as shown in Fig. 20.

Though granular V causes no crystal growth, it changes in shade to some extent, its dominant wavelength making a shift to the longer wavelength side by 0.9 mμ just as illustrated in Fig. 21. On the contrary, its isomer, granular VI causes no crystal growth and scarcely changes in its shade at all, as shown in Fig. 22. It can be said that the effect of chlorine atoms at 3,6- or 4,5-positions on the color change is the same as far as tetrachloro- and octachloro-compounds are concerned.

Fig. 23 shows the color change of granular VII. As the degree of chlorination becomes higher, the color change caused by heating in trichlorobenzene tends to diminish, but even VII exhaustively chlorinated changes its shade to some extent and its dominant wavelength shifts to the longer wavelength side by 1.9 mμ with an increase in yellowishness. However, there is no such crystal growth here as is observed in the case of granular II and III.

Compared with the chlorine atoms of 4,5-positions, those of 3,6-positions have scarcely any power of checking the crystal growth in organic solvents, but they are very powerful in shifting their dominant wavelength to the longer wavelength side. The dominant wavelengths of granular III and its isomer, granular IV are 481.5 mμ and 478.3 mμ respectively, which show that chlorine atom of 3-position is more influential in making an increasing of yellowishness than that of 4-position. This is also the case with granular V and its isomer, granular VI. That is, the former has a dominant wavelength of 485.0 mμ while the latter one of 482.5 mμ.

(3) *X-ray diffraction patterns of pigments.*— X-ray diffraction patterns obtained with a recording X-ray apparatus are shown (Fig. 24 to Fig. 40).

Fig. 24 shows the needle-formed I prepared by sublimation and Fig. 25 shows the granular II prepared from the solution of I in 98% sulfuric acid through reprecipitation method. What is common to both of them is the line of 7°, but they have nothing in other respects. I has the second and third strongest lines at 9° and 23.6°, but II has them at 27.6° and 26.8°; this indicates that there is a great difference between the two forms.

Figs. 26 and 27 show respectively III in needle form as well as in granular form. Fig. 28 shows granular III boiled in trichlorobenzene for 10 hr. The line of 6.4° is the only point in

common to Figs. 26 and 27. When the granular product is boiled in trichlorobenzene, its diffraction pattern changes as shown in Fig. 28, approaching that of the needle product (Fig. 26). This phenomenon perfectly coincides with the shade change exhibited by reflectance curves and the form change exhibited by electron microscopic photos.

Figs. 29 and 30 show respectively IV in needle form as well as in granular form. Fig. 31 shows the granular IV boiled in trichlorobenzene for 10 hr. What is common to Figs. 29 and 30 is the neighborhood of 6°. In the needle product, the second, third and fourth strongest lines are found at 9°, 23.6°, and 26°, but in the granular product they are at 26.8°, 26.4° and 13.2°, no similarity being found between the two forms. The granular product, if boiled in trichlorobenzene, changes to some extent and, judging from the diffraction pattern (Fig. 29), approaches the needle product, as shown in Fig. 31.

The X-ray diffraction pattern of needle-formed IV (Fig. 29) closely resembles that of needle-formed I (Fig. 24), but needle-formed III (Fig. 26) differs from needle-formed I. Granular IV (Fig. 30) and granular III (Fig. 27) show different patterns as is the case with the needle forms. Between III and IV, no similarity is found either in needle forms or in granular forms.

Figs. 32 and 33 show respectively V in needle form as well as in granular form. Fig. 34 shows the granular V boiled in trichlorobenzene for 10 hr. In Fig. 32 the strongest line is at 6° and the second and third strongest lines at 27.2° and 8° respectively. In Fig. 33 such lines are at 26.4°, 6.4° and 5.8° respectively, but no similarity is found between the two forms. When the granular product is boiled in trichlorobenzene, a diffraction pattern very similar to the needle form (Fig. 32) is obtained as shown in Fig. 34.

Figs. 35 and 36 show respectively VI in needle form as well as in granular form. Fig. 37 shows the granular VI boiled in trichlorobenzene for 10 hr. In Fig. 35 the strongest line is at 6.4° and the second and third strongest lines at 30.4° and 15.2°. In Fig. 36 such lines are at 30.4°, 15° and 6.8° respectively. Though there is no similarity between the two forms, their X-ray diffraction patterns are considerably closer to each other than those of I, II, III, IV and V. The granular product has no line at 52.4° which is in the case of the needle product. But, when it is boiled in trichlorobenzene, 52.4° line appears and the tendency of approaching the X-ray diffraction pattern of the needles product (Fig. 35) is also recongnized. On the other hand, no similarity is found between V and VI; this fact reminds us of the relation of III to IV. Thus, the influence of the position of chlorine upon the crystal structure is quite evident.

Figs. 38 and 39 show respectively VII in needle form as well as in granular form. Fig. 40 shows the granular VII boiled in trichlorobenzene for 10 hours. In Fig. 38 the strongest line at 6.8° and the second and third strongest lines at 31.6° and 6.2°. In Fig. 39 such lines are at 26.4°, 11.6° and 5.6° respectively. Thus there is no similarity between the two forms. When the granular product is boiled in trichlorobenzene, the strongest line is at 26.8° and the second and third strongest lines at 26.4° and 25.9°, showing a tendency of approaching the X-ray diffraction pattern of the needle product, just as in the case already described.

Discussion

(1) Polymorphism of Copper Phthalocyanine and its Chlorinated Derivatives.—It has been obvious that copper phthalocyanine and copper monochlorophthalocyanine have two forms of crystal structures. The author could make it clear that, chlorinated copper phthalocyanine have two form of crystal structures, no matter how large or small the chlorine contents may be.

This fact must be verified for copper phthalocyanines that their chlorine numbers ranges from naught to sixteen. These chlorinated copper phthalocyanines are to be obtained from mono-, di- and trichlorophthalic anhydrides with chlorine atoms at definite positions and tetrachlorophthalic anhydride. But it becomes difficult for chlorinated derivatives of phthalic anhydride to react as the chlorine contents grow larger. To cite an example of the experiments by the author, in the formation of phthalocyanine from tetrachlorophthalic anhydride, dechlorination reaction occurred and copper hexadecachlorophthalocyanine the author aimed at was not obtained. Meanwhile, phthalocyanine formation was run on the mixture of a given amount of chlorinated phthalic anhydrides, but it was not confirmed whether they reacted uniformly or singly. Consequently, this experiment was discontinued and examination was done with the six kinds of samples listed above. The aimed object was satisfactorily achieved by the results with them.

(2) Crystal Growth of Chlorinated Copper Phthalocyanines.—It is known that the introduction of chlorine atoms into copper phthalocyanine can prevent the crystal growth in organic solvents. Particularly, no crystal growth is recognizable in copper phthalocyanine green with a large chlorine content, but the position of chlorine atom plays an important role in crystal growth of lowly chlorinated compounds. Namely, chlorine atom at 4-position gives forth a very great action

in suppressing the crystal growth but the one at 3-position gives hardly any effect.

When more than eight chlorine atoms are contained, crystal growth is not usually recognized. But, if boiled in such high boiling point organic solvent as trichlorobenzene, all the X-ray diffraction patterns of the products where no crystal growth is recognized tend to approach those of the needle products. This phenomenon is similar to the transformation of unstable β-form copper phthalocyanine into stable α-form by heating the former in organic solvents.

The author gratefully acknowledges the instruction of Dr. Ryozo Goto, Professor of Kyoto University, Dr. Teruichiro Kubo, Professor of Tokyo Institute of Technology, Dr. Takahisa Nakamura and Dr. Wataru Ishikawa, Toyo Ink Mfg. Co. The author's thanks are also due to Mr. Seiki Kato, Tokyo Institute of Technology, for carrying out the X-ray analysis.

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Study on Zinc Oxide-Chromium Oxide Catalyst. IV. Dependency of Catalytic Activity on Catalyst Structure

By Yoshisada OGINO, Masaaki OBA and Hiroshi UCHIDA

(Received November 13, 1958)

Our previous paper[1] reported that chromium oxide in a catalyst for methanol synthesis played two roles of promoting actions, intercrystalline on the one hand, and intracrystalline on the other hand. For the purpose of understanding the promoting actions from a structural viewpoint of the catalyst, this study has been made, and presents results on catalyst structures such as the crystal- and the macroscopic geometrical structure. On the basis of available data, the relationship between the catalytic activity and the catalyst structure is considered.

Taking the information thus obtained into consideration, we have attempted to prepare a catalyst of the higher activity for the methanol synthesis.

Experimental

Specimens of the same catalysts as described in our previous paper have been used in the present study. The catalysts were divided into three groups, catalysts A, B, and a catalyst S. A catalyst of the first group was a direct preparation from a paste of zinc oxide powder kneaded with a chromic acid solution, while one of the second group was produced from the solid matter remaining after washing of the paste with acetone. This last was prepared from a residue obtained by treating a reduced preparation of catalyst B with nitric acid. Table I shows Cr/Zn ratio determined for each catalyst, with its denotation. The previous paper[1] reported their catalytic activities for the methanol synthesis and decomposition, together with specific surface areas after reduction.

Part of the catalysts, both the raw and the reduced ones, were subjected to an X-ray study by means of a Geiger-counter spectrometer using filtered copper K_α ray.

Experimental data for the specific surface areas were supplemented with those determined on the raw catalysts by the BET method. From an extent of the surface area S, an average diameter d of particles in the catalyst granules was calculated by the aid of the relation of $d=6/(\rho S)$, where ρ was a catalyst density determined by the water-displacement method. Moreover, pore size distributions in three reduced preparations of the catalysts were determined by applying Barret's method[2] to nitrogen desorption isotherms at -195°C.

Experimental Results

Crystal Structure from X-ray Diagram. —Catalyst structures as revealed by X-ray diagrams are listed in Table II. Even the raw catalysts of a very low chromic

1) Y. Ogino, M. Oba and H. Uchida, This Bulletin, **32**, 284 (1959).

2) E. P. Barret, L. G. Joyer et al., *J. Am. Chem. Soc.*, **73** 373 (1951).

TABLE I. CHEMICAL COMPOSITION OF THE CATALYST

Catalyst	A-0	A-1	A-2	A-3	A-4	A-5	A-6
Cr/Zn ratio	0	0.05	0.10	0.18	0.25	0.33	0.40
Catalyst	—	B-1	B-2	—	B-4	B-5	B-6
Cr/Zn ratio	—	0.05	0.09	—	0.23	0.31	0.36
Catalyst	A-7	A-8	A-9	A-10	A-11		
Cr/Zn ratio	0.50	0.67	1.00	1.10	1.50		
Catalyst	B-7	B-8	B-9	B-10	B-11		
Cr/Zn ratio	0.38	0.47	0.50	0.50	0.50		

TABLE II. CRYSTALLITES IN RAW CATALYSTS FROM X-RAY DIAGRAMS

Catalyst	Crystallites	Catalyst	Crystallites
A-2	ZnO(s), II_β, II_α, III_β	B-2	ZnO(s), II_β, II_α, III_β
A-6	I_β	B-4	ZnO(w), II_β, II_α, III_β
A-7	I_β	B-5	ZnO(very w), II_β(b)
A-9	complicated pattern	B-7	I_β
A-10	probably of Zn bichromate	B-8, -9, -11	I_β

s, strong: w, weak: b, broad.

acid content (catalysts A-2, B-2) give diffraction patterns of zinc-hydroxychromates, such as III_β, II_α and II_β besides the strong pattern of zinc oxide[3]. As the chromic acid content increases, the pattern due to I_β begins to appear in place of the foregoing hydroxychromates, and that due to zinc oxide becomes weaker, disappearing finally (catalysts B-4, -5). The diagrams taken of catalysts B-7, -8, -9 and -11 of the highest chromic acid content (Cr/Zn ratio of 0.5) among the catalysts of to B series show only the sharp pattern due I_β, whereas the one taken of catalyst A-7 of the same Cr/Zn ratio gives, besides the above, a complicated pattern, which appears stronger in the diagram taken of catalyst A-8. The complicated one seems to refer to zinc bichromate, and presumably comes from the solid layer of a much higher chromic acid content which the liquid in the paste has left behind on the original solid particles (refer to 1).

The crystal structure of the catalyst is appreciably altered by reduction. Although the diagrams taken of the raw catalysts give patterns of various kinds of zinc-hydroxychromates and bichromate, those taken of the reduced catalysts give only two kinds of patterns referring to zinc oxide and zinc chromite spinel. Within a range of Cr/Zn ratio less than 0.5, the pattern of zinc oxide becomes the weaker and the broader for the increaing Cr/Zn ratios, whereas that of zinc chromite maintains a definite degree of broadening, notwithstanding the fact that the intensity is increasing. Catalyst A-10 of a high Cr/Zn ratio gives much sharper patterns of both kinds, and catalyst S, though it has a Cr/Zn ratio (1.6) a little less than the stoichiometric ratio (2) of zinc chromite spinel, gives the pattern due to zinc chromite spinel alone[5].

Rough calculations of linear dimensions D of zinc oxide and zinc chromite spinel crystallites have been made by the aid of Scherrer's formula, $D = k\lambda/\beta\cos\theta$, where k is a constant approximately 0.9, λ is wave length of an X-ray, β is diffraction breadth of a line, and θ is Bragg angle. In the calculation, respective (102) and (400) reflections of zinc oxide and zinc chromite spinel were employed.

In Fig. 1 linear dimensions of crystallites of zinc oxide and zinc chromite spinel are plotted as a function of Cr/Zn ratio, respectively. As Cr/Zn ratio increases, the crystallite size of zinc oxide which originally was as large as 500 Å in linear dimension diminishes rapidly. In this respect, the crystallites of zinc chromite spinel contrast sharply with the above, the linear dimension being kept within a narrow range of 60~100 Å. With an addition of the further increasing amounts

3) By Feitknecht et al.[4], the diffraction patterns as well as chemical formulae of zinc-hydroxychromates were given. The formulae are as follows:
III_β: $ZnCrOr_4 \cdot 3Zn(OH)_2 \cdot 4Zn(CH)_2$, II_α: $ZnCrO_4 \cdot 2.5\,Zn(OH)_2 \cdot 2H_2O$, II_β: $ZnCrO_4 \cdot 2.5Zn(OH)_2$, I_β: $ZnCrO_4 \cdot Zn(OH)_2$

4) W. Feitknecht and L. Hugi-Carmes, *Helv. Chim. Acta.*, **37**, 2107 (1954).

5) Our results have revealed more kinds of zinc-hydroxychromates than those found by Kawamura et al.[6] with their catalysts, which they prepared by a little different procedure from ours.

6) M. Kawamura, T. Irie, Y. Shiraishi et al., *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **60**, 162 (1957).

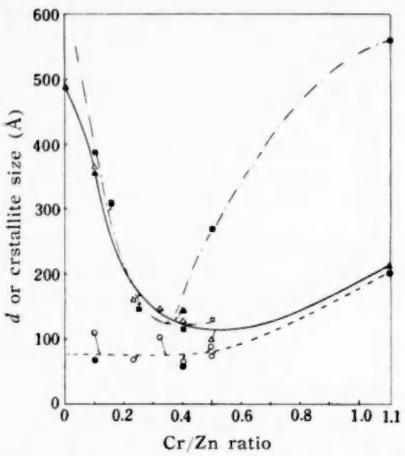


Fig. 1. Average particle diameter and crystallite size as function of Cr/Zn ratio.
—·—·—, average particle diameter: ——, size of ZnO crystallite: ·····, size of zinc chromite spinel crystallite. ●▲■, catalyst A: ○△□, catalyst B.

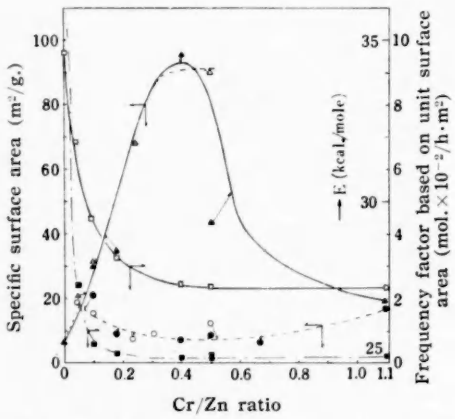


Fig. 2. Specific surface area, activation energy, and frequency factor as function of Cr/Zn ratio.
specific surface area: ●, raw catalyst (catalyst A), ○, (B), ▲, reduced catalyst (A), △, (B). □, activation energy for the synthesis, ■, frequency factor

of chromic acid beyond a Cr/Zn ratio of 0.5, the crystallites of both kinds grow to quite large ones.

Specific Surface Area and Average Size of Particles. — Specific surface areas of the raw catalysts as well as those of the reduced ones are shown as the function of Cr/Zn ratio in Fig. 2. Change in the areas of the former is small, the areas ranging from 7 to 20 m²/g., while the one in the area of the latter gives a remarkable peak at a Cr/Zn ratio of about 0.4~0.5, where the areas are five to ten times larger than those of the corresponding raw catalysts.

Granules of the raw catalysts are built up of particles as large as 1000~3000 Å in diameter. After reduction, the average size of the particles diminishes more or less remarkably according to chromic acid contents in the catalysts. Fig. 1 presents also the relationship between them. It shows that in a range of Cr/Zn ratio, less than 0.4, an average size of the particles is approximatly equal to the size of zinc oxide crystallites, and that in a range of higher Cr/Zn ratio, the particles are of much larger size than the crystallites of zinc oxide as well as zinc chromite spinel. The latter fact indicates that a particle is made up of a number of crystallites.

The growth of the particles as well as the crystallites, appearing in the catalysts of higher Cr/Zn ratios than 0.5, may be ascribed to thermal sintering[7] due to the glowing phenomenon that was once pointed out by Kawamura et al.[8] The glow has been found actually in the catalyst bed

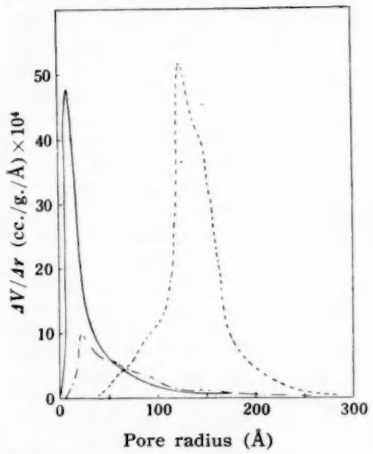


Fig. 3. Pore size distribution.
——, catalyst A-6: —·—·—, A-2: ····, A-10.

7) An assumption is also possible that crystallites of zinc chromite spinel are apt to aggregate with each other to become a large one, since there are not such a large number of zinc oxide crystallites as would be sufficient to prevent the aggregation. However, the assumption can not explain the simultaneous growth of zinc oxide crystallites.

8) M. Kawamura and T. Irie, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **60**, 166 (1957).

during reduction tending to appear more readily in the catalysts of the higher Cr/Zn ratios. It necessarily accompanies the growth to a greater extent.

Pore Size Distribution.—The results are shown in Fig. 3. Volumes of pores smaller than 300 Å in radius are 0.0588, 0.1178 and 0.2814 cc./g. for catalysts A-2, -6 and -10, respectively. A greater pore volume is not always associated with a larger extent of specific surface area, but the greater pore volume of extremely small pores with the larger extent of specific surface area.

Discussion

Intercrystalline Promoting Action of Chromium Oxide.—The intercrystalline promoter is a structural one responsible for production of a high-area structure. In this study, experimental evidences have been presented that a marked increase in the specific surface area takes place after reduction of the catalyst, and that well-grown particles of zinc-hydroxychromates in the raw catalysts disintegrate after reduction into extremely fine particles, which are often as small as the individual crystallites of zinc oxide and zinc chromite spinel[9], provided that scarcely any glow phenomenon has occurred during reduction. It has thus appeared that the formation of large particles of zinc-hydroxychromates in the raw catalysts is a requisite necessary for production of the extremely fine particles in the reduced catalysts, namely for the intercrystalline promotion of the activity by a chromic acid addition.

This picture[10] of structures of the raw and the reduced catalysts is consistent with the observations made by Matsui[12] on preparations of zinc-hydroxychromate II$_\beta$ and its thermal decomposition products under an electron microscope. In his observations, the crystallites (100~500 Å, 500~600 Å in diameter for zinc chromite spinel and zinc oxide, respectively) were much larger in size than the ones defined in the present study. This may have been due mainly to a higher temperature (500°C), at which zinc-hydroxychromate II$_\beta$ was decomposed, than to the reduction temperature in our study.

Compensation Effect in Catalytic Reactions[13].—We have found that catalyst S consists of zinc chromite spinel alone, and that a surface of the reduced zinc oxide-chromium oxide catalysts contains only two kinds of crystallites, crystallites of zinc oxide and zinc chromite spinel. As a consequence of the findings, we can expect according to the statement by Cremer[14] the compensation effect at the catalytic reactions on a series of the catalysts, under a reasonable assumption that crystallites of the different kinds simultaneously act as sites of a catalytic reaction[15]. On the other hand, the findings lead to the following expression of the intracrystalline promoting action of chromium oxide[1]; namely both the activation energy and the frequency factor based on unit surface area simultaneously fall with increasing proportions of zinc chromite spinel in the surface, the highest levels being thore of zinc oxide and the lowest levels being those of zinc chromite spinel (refer to Fig. 2). The expression coincides with the concept of the compensation effect by Cremer.

According to the aforegoing concept, an overall rate constant, k, is given by

$$k = F_1 A_1 \exp(-E_1/RT) + F_2 A_2 \exp(-E_2/RT) \quad (1)$$

where F is a fraction of the surface, subscripts 1 and 2 mean zinc oxide and zinc chromite spinel, respectively, and hence F_1 and F_2 stand for fractions of the surface occupied by zinc oxide and zinc chromite spinel, respectively. E is an activation energy, and A is a frequency factor based on unit surface area. Moreover, the finding in this study presents the following relationship,

$$F_1 + F_2 = 1 \quad (2)$$

As each value of A_1, A_2, E_1 and E_2 has already been known (refer to 1), F_1 and F_2 for any catalyst of the series can be evaluated from Eq. 1 and 2 by employing a value of k at a high temperature.

9) Comparatively large values of both the zinc oxide crystallite size and the average particle size determined for the catalysts of low Cr/Zn ratios are due to the presence of original large crystals of zinc oxide which have not been brought to a reaction with chromic acid.

10) The picture dose not exactly agree with the one for our previous catalysts[11], which were prepared by a somewhat different procedure from the present one.

11) H. Uchida and Y. Ogino, This Bulletin, **29**, 587 (1956).

12) T. Matsui, *J. Research Inst. Catalysis, Hokkaido University*, **4**, 109 (1956).

13) In this study the reactions include the methanol synthesis and decomposition.

14) E. Cremer, "Advances in Catalysis", Vol. VII, Rheinhold Publishing Corporation, New York (1956), p. 85.

15) According to the statement by Cremer, the compensation effect can be expected at the catalytic reactions on a series of the catalysts whose surface contains different activation energies, and in which the proportions of the sites are shifted with the chemical composition.

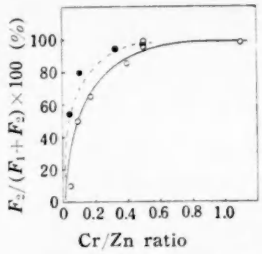


Fig. 4. Fraction of surface occupied by zinc chromite spinel as function of Cr/Zn ratio.
○, calculated from rate constant of synthesis, ●, calculated from rate constant of decomposition.

The results are shown in Fig. 4 as plots of $F_2/(F_1+F_2)$ vs. Cr/Zn ratio. This suggests migration of chromium ions from the particle interior into the surface taking place during reduction of the catalyst, but we can say nothing decisive in this respect as yet.

Attempt to Prepare Catalyst of Higher Catalytic Activity.—From the result that zinc chromite spinel yielded the lowest activation energy of the synthesis, it occurred to us first that a catalyst made of the spinel would be expected to give high activity, if it were provided with a large extent of surface area. However, an addition of chromic acid excessive to the amount corresponding to I_β always caused considerable decline in the surface area due to glowing in reduction. In this connection, we have made various efforts, e.g., reduction processes in hydrogen containing appropriate amounts of steam, to carry out the reduction without the glowing, but with no success. Another procedure, the simultaneous precipitation of hydroxides of zinc and chromium from a mixed solution of the nitrates with ammonia, yielded a catalyst of the desired chemical composition, but scarcely any evidence of zinc chromite spinel has been found unless the precipitate was heated at temperatures higher than 600°C[16]. The heating reduced the activity to a large extent, and we were unsuccessful in putting our first expectation into practice.

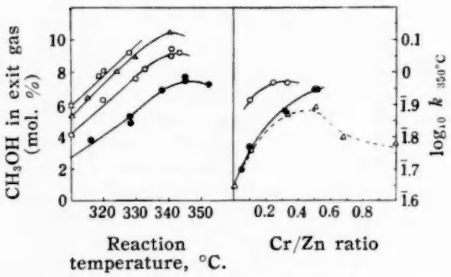
Our results[1] furthermore demonstrate that the specific catalytic activity, i. e., the activity based on unit surface area, for the methanol synthesis is increased appreciably by an addition of a small amount of chromic acid to such a level that is only a little lower than that of zinc chromite spinel. Natta[17], on the other hand, pointed out that zinc oxide produced by decomposition of zinc acetate was of a smaller crystallite size, and consequently showed higher activity than the usual ones. In view of the facts, it can next be expected that a catalyst of even a low chromic acid content may give higher activity, when it happens to have contained zinc acetate in the raw material. In producing a catalyst along with this expectation, the amount of chromic acid should be kept so low as not to provoke glowing during reduction, and hence a paste of the rather small Cr/Zn ratio of 0.25 has been chosen as a starting material, during the kneading of which appropriate amounts of acetic acid are added[18].

The results are given in Table IV, and Figs. 5A and 5B. A comparison of the

TABLE III. INCREASE IN SPECIFIC SURFACE AREA BY ACETIC ACID ADDITION

Catalyst	A-4	A-41	A-411	A-4111
CH_3COOH/ZnO (mol. ratio)	0	1/6	1/2	5/6
Specific surface area, m^2/g.	80	76	98	111
$k^{a)}\cdot 10^2$	6.9	10.1	12.4	14.2
$k/WS^{b)}\cdot 10^5$	7.75	10.5	10.0	8.3

a) a rate constant of the synthesis based on 10 cc. of the catalyst at 330°C.
b) the rate constant based on unit surface area.



Figs. 5A and 5B. Effect of acetic acid addition on catalytic activity.
A, synthesis. (left).
●, catalyst A-4, ○, A-41, △, A-II, □, A-4III.
B, decomposition. (right).
○, catalyst after acetic acid addition.
△, catalyst A, ●, catalyst B.

16) Even though the catalyst had not been heated at high temperatures, it could not give such a high activity for the methanol synthesis as the one obtainable with the catalyst in this study.

17) G. Natta, "Catalysis", Vol III, Rheinhold Publishing Corporation, New York (1955), p. 349.

18) By an acetic acid addition, the more violent glowing comes to take place.

table with the figures indicates a nearly parallel increase in the activities to the increasing extent of surface area. The figures disclose that the activity for decomposition rises more remarkably than the synthetic activity does. This leads to a premise that the addition of acetic acid does not result in surface enlargement of zinc chromite spinel, but results in that of zinc oxide whose synthetic activity is apt to decline rapidly with time (refer to 1). The premise can be confirmed from a constant value, 28.8 kcal./mol., of the activation energy of the synthesis independent of amounts of acetic acid added.

Summary

So far as catalysts made from pastes of zinc oxide powders kneaded with chromic acid solutions are considered, granules in the reduced ones are built up of extremely fine particles which usually are as small as individual crystallites of zinc chromite spinel as well as zinc oxide. The fine particles appear by way of the large particles of zinc-hydroxychromates in the raw catalysts. However, once the raw catalyst comes to contain a greater amount of chromic acid than that corresponding to zinc-hydroxychromate I_β, the granules in the reduced one are composed of the larger particles, an individual one of which is an assembly of a number of the crystallites.

On the basis of the results available on the catalyst structures, the intracrystalline promoting action of chromium oxide can be explained from Cremer's viewpoint of the compensation effect. The catalytic activity can be increased by adding an appropriate amount of acetic acid into the paste, the increase being nearly parallel to an increasing extent of the specific surface area. The increase by the addition, however, is expected only with the catalyst produced from the paste of a low chromic acid content.

The authors wish to express their sincere thanks to Messrs. S. Kato and M. Taniguchi of Tokyo Institute of Technology for their taking X-ray diagrams.

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The Normal Vibrations of Methanesulfonate Ion

By Kuniaki FUJIMORI

(Received October 28, 1958)

In the preceding paper[1] the infrared spectra of *n*-alkane-1-sulfonates were investigated and it was found that two S–O stretching vibrations and C–S stretching vibration were in the rock salt region.

In this paper the normal vibrations of the methanesulfonate ion were calculated, assuming the Urey-Bradley's field as the intra-molecular potential. This calculation was treated as a five-body problem, supposing the methyl radical to be one particle.

Calculation of Normal Vibration

Molecular Shape.—It was assumed that the methyl radical was one particle and the molecular shape of the methanesulfonate ion was similar to that of chloroform, i. e., this ion had the symmetry property of C_{3v}. This assumption is not reckless under the first order approximation[2].

Intra-molecular Potential. — As intra-molecular potential, the following Urey-Bradley's field[3] is assumed

$$V=\sum V_{r_i}+\sum_{i>j} V_{\alpha_{ij}}+\sum_{i>j} V_{q_{ij}}$$

where

$$V_{r_i}=K'_i r_i \Delta r_i+\frac{1}{2}K_i(\Delta r_i)^2$$

$$V_{\alpha_{ij}}=H'_{ij} r^2 \Delta\alpha_{ij}+\frac{1}{2}H_{ij}(r_{ij}\Delta\alpha_{ij})^2$$

1) K. Fujimori, This Bulletin, in press.

2) A. Simon and H. Kriegsmann, *Chem. Ber.*, **89**, 1718 (1956).

3) H. C. Urey, C. A. Bradley, *Phys. Rev.*, **38**, 1969 (1931).

$$V_{q_{ij}}=F'_{ij}q_{ij}\Delta q_{ij}+\frac{1}{2}F_{ij}(\Delta q_{ij})^2$$

and

K_i and K'_i: stretching force constants
H_{ij} and H'_{ij}: bending force constants
F_{ij} and F'_{ij}: repulsive force constants
r_i: distance between the central atom and the i-th atom
q_{ij}: distance between non-bonded atoms
r^2_{ij}: equals r_ir_j
α_{ij}: valence angle.

G and F Matrixes.—The G and F marixes of this molecule were made by Wilson's method[4] and were factored by symmetry property of C_{3v}[5]. The following elements were obtained.

a) A_1 type vibration (totally symmetric vibration).—i) Elements of G matrix

$$g_{11}=\mu_S+\mu_R \qquad g_{22}=-\frac{1}{3}\mu_S+\mu_O$$
$$g_{12}=-\frac{1}{\sqrt{3}}\mu_S \qquad g_{23}=\frac{4}{3}\mu_S$$
$$g_{13}=-\frac{4}{\sqrt{3}}\mu_S \qquad g_{33}=\frac{16}{3}\mu_S+2\mu_O$$

ii) Elements of F matrix

$$f_{11}=K_{S-R}+3t^2_{R-O}F'_{R-O}+3s^2_{R-O}F_{R-O}$$
$$f_{12}=\sqrt{3}\,(-t_{O-R}t_{R-O}F'_{R-O}+s_{R-O}s_{O-R}F_{R-O})$$
$$f_{13}=\frac{\sqrt{3}}{2}\,(t_{R-O}s_{O-R}F'_{R-O}+t_{O-R}s_{R-O}F_{R-O})$$
$$f_{22}=K_{S-O}+t^2_{O-R}F'_{R-O}+s^2_{O-R}F_{R-O}+4s^2_{O-O}F_{O-O}$$
$$f_{23}=\frac{1}{\sqrt{2}}\{(t_{O-R}s_{R-O}F'_{R-O}+t_{R-O}s_{O-R}F_{R-O})\sigma-2t_{O-O}s_{O-O}(F'_{O-O}+F_{O-O})\}$$
$$f_{33}=\frac{1}{2}\{(H_{R-S-O}-s_{R-O}s_{O-R}F'_{R-O}+t_{R-O}t_{O-R}F_{R-O})\sigma^2+(H_{O-S-O}-s^2_{O-O}F'_{O-O}+t^2_{O-O}F_{O-O})\}+\frac{3}{\sqrt{8}}\kappa/r^2_{S-O}$$

b) E type vibration (doubly degenerated vibration).—i) Elements of G matrix

$$g_{11}=\frac{4}{3}\mu_S+\mu_O$$
$$g_{12}=-\frac{\sqrt{2}}{3}\left(\frac{3}{\sigma}+1\right)\mu_S$$
$$g_{13}=\frac{4\sqrt{2}}{3}\mu_S$$
$$g_{22}=\mu_O+\left(\frac{1}{\sigma}\right)^2\mu_R+\frac{1}{6}\left(\frac{3}{\sigma}+1\right)^2\mu_S$$
$$g_{23}=-\frac{2}{3}\left(\frac{3}{\sigma}+1\right)\mu_S+\frac{1}{2}\mu_O$$
$$g_{33}=\frac{8}{3}\mu_S+\frac{5}{2}\mu_O$$

ii) Elements of F matrix

$$f_{11}=K_{S-O}+t^2_{O-R}F'_{R-O}+s^2_{O-R}F_{R-O}+3^2t_{O-O}F'_{O-O}+s^2_{O-O}F_{O-O}$$
$$f_{12}=(t_{O-R}s_{R-O}F'_{R-O}+t_{R-O}s_{O-R}F_{R-O})\sigma$$
$$f_{13}=-t_{O-O}s_{O-O}(F'_{O-O}+F_{O-O})$$
$$f_{22}=(H_{O-S-R}-s_{R-O}s_{O-R}F'_{R-O}+t_{R-O}t_{O-R}F_{R-O})\sigma+\left(\frac{1}{\sqrt{8}}\right)\kappa/r^2_{S-O}$$
$$f_{23}=-\frac{\sqrt{2}}{2}\kappa/r^2_{S-O}$$
$$f_{33}=(H_{O-S-O}-s^2_{O-O}F'_{O-O}+t^2_{O-O}F_{O-O})+\frac{1}{\sqrt{8}}\kappa/r^2_{S-O}$$

where the following notations are used;

κ(intra-molecular tension)
$=-(K'_ir^2_{ij}+F'_{q_{ij}}r_{ij}q_{ij}\sqrt{t_{ii}t_{ji}})$
$\sigma=r_{R-S}/r_{S-O}$, $\quad s_{ij}=(r_i-r_j\cos\alpha_{ij})/q_{ij}$
$s_{ji}=(r_j-r_i\cos\alpha_{ij})/q_{ij}$, $\quad t_{ij}=r_j\sin\alpha_{ij}/q_{ij}$
and $t_{ji}=r_i\sin\alpha_{ij}/q_{ij}$

and μ_S, μ_O and μ_R are reciprocals of atomic weights for sulfur, oxygen and the methyl radical, respectively.

Constants Used in Calculation.—*a) Nuclear distances.*—

S–O : 1.50 A[6]
S–R : 1.80 A*

b) Valence angles.—Valence angles for O–S–O and R–S–O are assumed to equal the tetrahedral one, that is 109°28′.

c) Force constants.—K_{S-O}, H_{O-S-O} and F_{O-O} are taken from those for sulfate ion[8], and K_{R-S} is taken from H_{Me-S} of dimethyl sulfide[9]. H_{R-S-O} is taken from the mean of H_{O-S-O} for sulfate ion and $H_{CH_2-S-CH_2}$ for diethyl sulfide[9]. F_{R-O} is taken from the mean of F_{O-O} for sulfate ion and F_{Me-Me} for tetramethyl silane[8]. κ_{MeSO_3} is taken

4) E. B. Wilson, *J. Chem. Phys.*, **7**, 1047 (1939); **9**, 76 (1941).
5) T. Shimanouchi, *Bulletine Inst. Phys. Chem. Research Tokyo (Riken Iho)*, **21**, 825 (1942).
6) A. Simon and H. Kriegsmann, *Z. Phys. Chem.*, **209**, 369 (1955).
* Summation of Pauling's covalent radii of single carbon and sulfur[7].
7) L. Pauling, "The Nature of the Chemical Bond", Cornell Univ. Press, Ithaca, N. Y. (1940), p. 164.
8) T. Shimanouchi, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **74**, 225 (1953).
9) M. Hayashi, ibid., **77**, 1962 (1956).

from the mean of $\kappa_{SO_4^{2-}}$ and $\kappa_{Si(CH_3)_4}$[8]. F' is assumed to be $-1/10\ F$[8]. In Table I values of these force constants are given.

TABLE I. FORCE CONSTANTS

F. C.	(dyn./cm.)$\times 10^5$	F. C.	(dyn./cm.)$\times 10^5$
K_{S-O}	6.01	F'_{O-O}	−0.076
K_{S-R}	3.01	F_{O-R}	0.397
H_{O-S-O}	0.43	F'_{O-R}	−0.0397
H_{O-S-R}	0.294	κ	0.328*
F_{O-O}	0.76		

* Unit is (dyn./cm.)$\times 10^{-11}$.

Results, Assignment and Comparison with Observed Data

As the results of calculation, the following values were obtained:

$\nu_1 = 788\ cm^{-1}$ $\nu_2 = 1002\ cm^{-1}$ $\nu_3 = 538\ cm^{-1}$

$\nu_4 = 1081\ cm^{-1}$ $\nu_5 = 537\ cm^{-1}$ $\nu_6 = 367\ cm^{-1}$

Of these vibrations ν_1, ν_2 and ν_3 are totally symmetric and ν_4, ν_5 and ν_6 are doubly degenerated.

These values are compared with the results of Raman spectra of potassium methanesulfonate in aqueous solution studied by Simon and Kriegsmann[6]. Relatively strong lines which could not be considered as C–H stretching and C–H deformation vibrations, are as follows: 348 cm^{-1}(5b), 533 cm^{-1}(2), 560 cm^{-1}(4), 789 cm^{-1}(8), 1054 cm^{-1} (10) and 1184 cm^{-1} (2b). (Number in brackets are intensities of Raman lines.)

They attributed the lines at 789, 1054 and 1184 cm^{-1} to ν_1 (C–S stretching vibration), ν_2 (S–O stretching totally symmetric vibration) and S–O stretching antisymmetric vibration, respectively.

By comparing the author's calculation with observed infrared spectra[1], the assignments can be made as indicated in Table II.

The agreement between the calculated and the observed frequencies is satisfactory except for S–O stretching vibration. The reason will be attributed to the fact that the S–O stretching force constant is taken from that of sulfate ion.

TABLE II. COMPARISON OF CALCULATED AND OBSERVED VALUES (in cm^{-1})

Assignment	Raman	I. R.	Calcd. I	Calcd. II
C–S Stretching	789	789	788	789
S–O Stretching	1054	1060	1002	1055
Deformation	533		538	536
S–O Stretching	1184	1192	1080	1182
R–S–O Deformation	560		537	557
O–S–O Deformation	348		367	349

The force constants were corrected as indicated in Table III, using the trial and error method combined with the method of least squares[10]. If the calculation of normal vibration is done again using these corrected force constants, the agreement between the calculated and observed values becomes much more satisfactory. The calculated values are indicated in Table II as "Calcd. II".

TABLE III. CORRECTED FORCE CONSTANTS

F. C.	(dyn./cm.)$\times 10^5$	F. C.	(dyn./cm.)$\times 10^5$
K_{S-O}	7.31	F'_{O-O}	−0.065
K_{S-R}	3.05	F_{O-R}	0.34
H_{O-S-O}	0.552	F'_{O-R}	−0.034
H_{O-S-R}	0.26	κ	0.328*
F_{O-O}	0.65		

* Unit is (dyn./cm.)$\times 10^{-11}$.

The author wishes to express his indebtedness to Dr. A. Kotera, Professor of Tokyo University of Education, and Dr. T. Shimanouchi, Professor of the University of Tokyo, under whose kind direction this work was performed. And the author wishes to thank Mr. Y. Akai, Chief of Research Section of Funakawa Refinery, for his encouragement of this research.

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The Role of the Cationic Group in Anionic Detergents

By Maresuke KASHIWAGI and Heihachi EZAKI

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It seems that sodium salt of alkyl sulfate has been extensively studied, while little data are known concerning organic salts of alkyl sulfate. It is therefore thought to be of interest to investigate the effect of the substitution of the cationic group attached to the hydrophilic portion of the detergent molecule. Such effcts should be studied both surface-chemically and from the viewpoint of bulk properties.

Materials used for those investigations were, as sulfate type, triethanolamine dodecyl sulfate (TDS), morpholine DS (MDS), pyridine DS (PDS), and sodium DS. As sulfonate type, triethanolamine alkyl benzene sulfonate (TABS) and sodium salt of the same sulfonate (SABS) were used.

Experimental

Materials.—All dodecyl sulfates were synthesized from dodecyl alcohol, chlorosulfonic acid and the corresponding base. The way of synthesis and the identification of product was given in detail previously[1].

Alkyl benzene, the raw material for the sulfonated detergent was the product of Oronite Chemical Co. and was redistilled at 130~136°C/3 mmHg. It was sulfonated with pure chlorosulfonic acid, at an equimolar ratio assuming the alkyl chain of the alkane to be mainly isododecyl, and neutralized either with aqueous sodium hydroxide or triethanolamine. The analysis of SABS showed that the amounts of unreacted alkane and inorganic material were less than 1.5%, respectively.

Measurements.—Monolayer experiments were carried out with the use of a Wilhelmy-type surface balance and surface tension was measured with DuNuoy's instrument. Foaming power was measured, at 40°C throughout, by Ross-Miles method[2,3], apparent viscosity was measured, at 30°C, with a modified Couette type rotational viscometer. Because of their extremely high solubility, the yield of TDS and PDS decreased considerably in the process of purification and we could not carry out whole-scale solubility measurements. Therfore, a Kraft point conventionally determined by dye color change[4] was adopted as a measure of solubility, since this method requires only a very small amount of the sample. It appeared that the Rhodamine 6G used for this purpose fortunately gave a clear color change at the K. P.

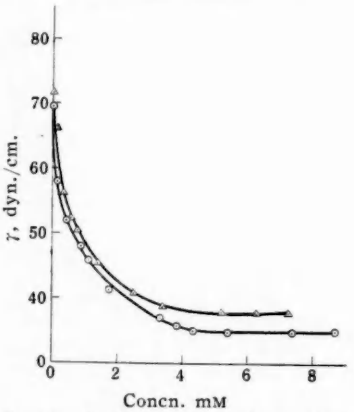

Fig. 1. Surface tension of organic DS.
—⊙— MDS 40°C
—△— TDS 33°C

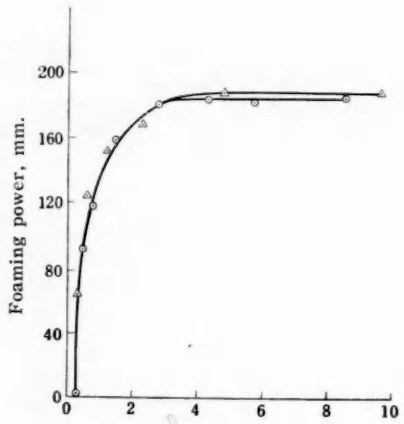

Fig. 2. Foaming power of TDS and MDS.
—⊙— MDS
—△— TDS 40°C

1) M. Kashiwagi, This Bulletin, **31**, 667 (1958).
2) M. Kashiwagi, ibid., **29**, 193 (1957).
3) M. Kashiwagi, ibid., **30**, 572 (1957).
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Results

1) **Substitution of the Cationic Group in Sulfate Portion.**—(*A*) *Surface Chemical Properties.*—(*1*) *Surface area.*—Surface areas of MDS, TDS and PDS on the substrate of 25% ammonium sulfate are calculated from $F-A$ curve and a surface equation of their state[5] developed by Pethica, $F(A-A_0)=nkt$, where A_0 refers to the surface co-area of the hydrophilic group in the molecule and n is a constant. A_0 is thus calculated to be 34 Å^2/mol., identical for all three DS', between the surface areas of 70 Å^2/mol. and 40 Å^2/mol. and, at 40 Å^2/mol., changes to 17 Å^2/mol. which corresponds to the cross-sectional area of the hydrocarbon chain. Those values of A_0 are in excellent agreement with those of SDS[5]. The reason for this coincidence is now ascribed to the shielding effect of ammonium ions fully present in bulk phase since the colloidal electrolyte of the detergent may be considered to be equally accessible to both ammonium and organic cations.

(*2*) *Surface tension.*—Surface tension vs. concentration curves of both TDS and MDS are shown in Fig. 1, from which values of CMC are determined to be 0.004 M for both detergents. The CMC value of SDS is known to be about 0.007 M[6]. This value (0.004 M) is the same in the order of magnitude, but somewhat smaller than that of SDS. This small discrepancy may be ascribed both to the relatively large size of the counter ion[7,8] and the greater ions degree of hydration of these ions[9].

(*3*) *Foaming power.*—Foaming power vs. concentration curves of TDS and MDS are shown in Fig. 2, from which values of CMC for both detergents can be determined[2] to be 0.004 M and 0.003 M respectively. These values of CMC can be considered to be in good agreement with the values from surface tension measurements, as appeared in Fig. 1. Anyway, those two salts of DS exhibit approximately the same degree of foaming power, and moreover this in turn proves to be nearly equal to the foaming power of 186 mm. shown by aqueous SDS at its CMC.

(*B*) *Bulk Properties.*—(*1*) *Solubility.*—Solubility values of organic salts of DS, except for MDS, are found to be much higher than those of SDS. Solutions of both TDS and PDS at 30% remainded perfectly transparent even at 0°C, while MDS alone has very small solubility at 0°C, evidently much less than its CMC (i. e., less than 0.15%). The kraft points (K. P.) of both TDS and PDS are found to be less than 0°C, whereas the K. P. of MDS is found to be 30°C, compared with 10°C of SDS[10]. Thus a striking difference in solubility by the nature of the cationic group is observed as estimated from K. P. data.

(*2*) *Viscosity.*—Viscosity values of TDS and SDS at 30°C are listed in Table I. It is clear that SDS exhibits much higher viscosity than organic DS.

TABLE I. VISCOSITY OF TDS AND SDS AT 30°C

	10%	20%	30%
TDS	1.5 c. poise	3	5
SDS	4.5	8.5	820

(II) Substitution of the Cationic Group in Sulfonate Portion.—Foaming power, of TABS in a standard condition (0.25%, 40°C) is 193 mm., while that of SABS under the same conditions is found to 196 mm. in the Ross-Miles unit. Those values nearly equal each other. The relation is, however, quite different in solubility. TABS dissolves in the amount of 80%, at 0°C, while the solubility of SABS is found to be less than 10% at 20°C. Viscosity values at 30°C are 7 cp. at 30%, 2.5 cp. at 20%, and 1.4 cp. at 10% solutions for TABS, while the viscosity of SABS is found to be 5 cp. at 10% solution. Once again those data may be interpreted as an indication that the substitution of the cationic group in sulfonate portion does not virtually change surface chemical properties, but it does change the bulk properties.

Discussion

The results thus obtained are summarized in Table II. The value of CMC obtained for TDS and MDS, as they appeared in Table II, are in the same order but smaller than that of SDS. It has been shown that the value of CMC decreases when the counter ion becomes very large[7], or the degree of hydration of the counter ion decreases[8,9]. The

5) B. A. Pethica, *Trans. Faraday Soc.*, **50**, 413 (1954).
6) E. G. Goette, *J. Colloid Sci.*, **4**, 459 (1949).
7) A. Cushman A. P. Brady and J. W. McBain, ibid., **3**, 425 (1948).
8) K. Meguro and T. Kondo, private communications.
9) K. Meguro et al., *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **77**, 1236 (1956).
10) E. Hutchinson, *J. Phys. Chem.*, **58**, 1126 (1954).

second factor would be less effective, because CMC values of potassium, sodium and lithium salts of DS are fairly close (7～10 mM)[9].

According to Klevens, these differences may be due to minor differences in the degree of ionization of the micelles, for it has been observed that the presence in small amounts of unionized additives (unreacted alcohol for example) will markedly decrease the CMC, whereas the use of an ionized additive of an equivalent chain length and the same charge will result in little change[11]. This is true of uni-univalent electrolytes. As for a polyvalent electrolyte, valence of cation may follow the Schulz-Hardy rule in decreasing CMC[12].

TABLE II. PROPERTIES OF VARIOUS SALTS OF DODECYL SULFATE

Surface properties

	TDS	PDS	MDS	SDS
Surface area of hydrophilic group on 25% $(NH_4)_2SO_4$	34Å²/mol.	34	34	34
Foaming power (0.25%, 40°C)	188 mm.	—	184	186
CMC	4mM		3～4	7

Bulk properties

	TDS	PDS	MDS	SDS
Kraft P.	less than -5°C	less than 0°C	30°C	10°C
Estimated solubility grade	1	2	4	3
Viscosity	low	low	low	high

Summary

Various salts of dodecyl sulfate (DS) and alkylbenzene sulfonate have been investigated surface-chemically and from the viewpoint of their bulk properties. It was shown that these organic salts of DS occupy the same surface area as that of SDS, on the substrate of concentrated anmonium sulfate, independent of the nature of the cationic group attached to the sulfate anion. CMC values determined by two different methods (i. e., surface tension and foaming power) show practically the same value. These results are approximately in accord with the known principle that the number of carbon atoms in the molecule of the normal straight chain colloidal electrolyte of one particular class is the determining factor for the value of CMC, although a slight but definite shift in CMC value is observed with variation in substituting group. On the other hand, bulk properties such as viscosity and solubility are influenced remarkably by the substitution of cationic group in anionic detergents.

The author wishes to thank Professor R. Matsuura of Kyusyu University for his kind advice.

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11) H. B. Klevens, ibid., **14**, 742 (1946).
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Polymerization of Aminoacetonitrile

By Hidesaburo HANAFUSA* and Shiro AKABORI

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If the protein is absolutely essential for all living things, the non-enzymic formation of protein must have been prerequisite for the origination of life.

In 1936 Oparin[1] postulated that α-amino acids could have been formed non-biologically from hydrocarbons, ammonia and hydrogen cyanide at the age of the earth when atmosphere contained these substances in high concentrations. Bernal[2] emphasized the role played by ultraviolet light in the formation of organic compounds at a certain stage of the evolution of the earth. He also suggested that life

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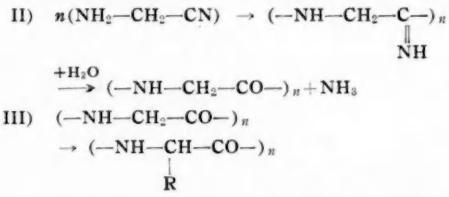
1) A. I. Oparin, "The Origin of Life", Macmillan Co. N. Y. (1936).

2) J. D. Bernal, "Physical Basis of Life", Routledge and Kegan Paul Ltd., London (1951).

might have originated on the surface of clay which accumulated large amounts of organic substances. Oparin's hypothesis has received strong experimental support from the recent work of Miller[3].

It has generally been accepted that the first proteins or fore-proteins were non-biologically formed by the polycondensation of preformed free amino acids. This belief is solely based on the fact that proteins in the present-day organisms are synthesized via free amino acids. Such non-biological formation of polypeptides and proteins, however, seems to be very difficult owing to the requirement of free energy, though Bresler[4] reported the reconversion of tryptic hydrolysates to the original proteins under an extremely high pressure.

In 1955 Akabori proposed[5] a hypothesis concerning the origin of the fore-protein and speculated that it must have been produced through reactions consisting of the following three steps.



The first step is the formation of aminoacetonitrile from formaldehyde, ammonia and hydrogen cyanide. The second is the polymerization of aminoacetonitrile on a solid surface, probably in the state adsorbed on clay, followed by the hydrolysis of the polymer to polyglycine and ammonia. The third step is the introduction of side chains into polyglycine by the reaction with aldehyde or with unsaturated hydrocarbons. The reaction in the first step is well known as Strecker's reaction. Akabori and co-workers[6] reported some experimental results on the possibility of the third step.

The present paper deals with experiments concerning the second step in the formation of the fore-protein, that is the polymerization of aminoacetonitrile. Although acetamidine is formed from ammonia and acetonitrile in methanol solution, the condensation of primary amine with nitrile has been known very little. In the synthesis of purine derivatives, Traube[7] synthesized diamino thiopyrimidine by the condensation of thiourea and malonitrile. In this reaction sodium ethoxide was used as catalyst, and the anhydrous condition had been kept in the course of reaction.

Aminoacetonitrile prepared by the usual method was heated at 120~140°C for 3~5 hr. in the presence of clay, which was used as adsorbent of the nitrile and seemed to play a role as catalyst in this reaction. The product was extracted with water, dilute hydrochloric acid and sodium hydroxide solution. The presence of glycyl-glycine and glycyl-diglycine in extract and partial hydrolysate of extraction residue was confirmed by paper and column chromatography.

Experimental

Materials.—*Aminoacetonitrile sulfate;* According to Anslow and King's method[8] aminoacetonitrile sulfate was obtained, m. p. 164°C (decomp.). *Kaolin;* Commercial "Kaolin" was refluxed with hot water. After 2 hr., it was centrifuged, washed with distilled water and dried in an air bath. Kaolin treated with concentrated hydrochloric acid was used in some cases. *Other clays;* Japanese acid clay and bentonite were treated in the same way as kaolin. *Glycyl peptides;* Gly-Gly** and Gly-Gly-Gly** were synthesized in our laboratory and the purity was confirmed on paper chromatogram.

Procedures.—Several procedures were tried for polymerization of aminoacetonitrile. A typical method is the following.

One gram of amino acetonitrile sulfate was mixed with 20 times of kaolin and heated at 130~135°C for five hours. To heat uniformly, the mixture was taken in a wide bottomed flask and kept in an air bath at 130°C. As the liberation of ammonia was detected in the course of reaction, the top of flask was connected with a small tube of Dowex-50 (H-form). The reaction mixture, being of violet-grey color, was extracted with each 30 ml. of water, N/10 hydrochloric acid and N/10 sodium hydroxide successively in the cold (see Fig. 1). The pH of the water extract was about 5.5, and each of extracts showed a strong positive biuret reaction. A part of the residue was hydrolyzed with N/10 hydrochloric acid at 100°C for 1 hr. (KB) and another part was

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4) E. S. Bresler et al., *Izvest. Akad. Nauk, SSSR, Ser. Biol.*, **13**, 392 (1949).
5) S. Akabori, *Kagaku* (*Science in Japan*), **25**, 54 (1955).
6) S. Akabori, K. Okawa and M. Sato, This Bulletin, **29**, 608 (1956).
7) W. Traube, *Ann. Chem.*, **331**, 64 (1904).
** Glycine, glycyl-glycine and glycyl-diglycine are abbreviated as Gly, Gly-Gly, Gly-Gly-Gly, respectively.
8) W. K. Anslow and H. King, *J. Chem. Soc.*, **1929** 2463.

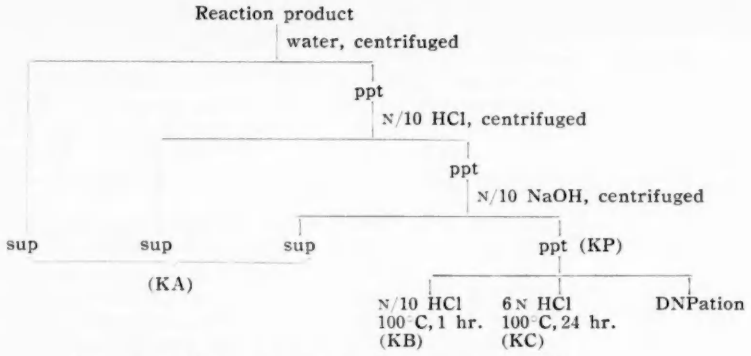

Fig. 1. The Scheme of extraction of reaction product

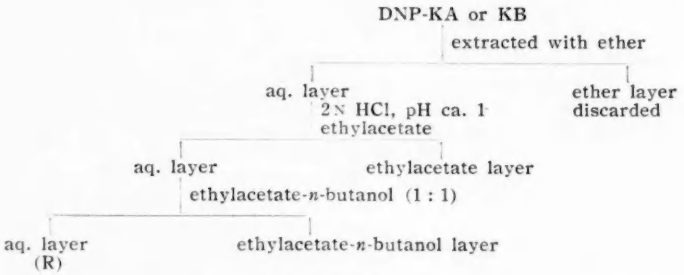

Fig. 2. Procedure for the extraction of DNP-peptides.

hydrolyzed with 6N hydrochloric acid at 100°C for 24 hr. (KC). For the purpose of the hydrolysis of imino group of polymerized product, combined extract (KA) was refluxed at pH 1 for 1 hr. After neutralization the component of each fraction was examined by paper chromatography and by paper and column chromatography after dinitrophenylation.

The Component of Product. — After concentration, an aliquot of each fraction was chromatographed on filter paper using 80% phenol as solvent. From this paper chromatogram, it was found that each fraction contained glycine, and KA and KC contained also glycyl peptide, probably Gly-Gly and Gly-Gly-Gly. These findings were confirmed by dinitrophenylation technique. This method is excellent for the reason that non-peptide basic substance which is ninhydrin positive can be separated from dinitrophenylated (DNP-) glycyl peptide. After each fraction was dinitrophenylated by the usual method, DNP-peptides were extracted with ethylacetate and *n*-butanol as shown in Fig. 2. Ethylacetate extract and ethylacetate-*n*-butanol extract were combined and dried in vacuo. After removing dinitrophenol by sublimation using cold-finger condenser[9], a part of this DNP-peptide fraction was subjected to one-dimensional chromatography on filter paper using *n*-butanol saturated with 1% ammonia as solvent. Several spots of R_f values 0.30, 0.17, 0.11 and lower ones were obtained; the first three spots were identified as DNP-derivatives of Gly, Gly-Gly and Gly-Gly-Gly in comparison with standard samples. Another part of the DNP-peptide fraction was chromatographed on a buffered celite column by a partly modified Perrone's method[10]. The solvent system used was ethylacetate-0.5M phosphate buffer (1:1). After 10 parts of celite were mixed with 6.6 parts of the lower layer of the solvent mixture, celite was poured into the column of 20 cm. high and 2 cm. in diameter with the upper layer of solvent and packed with glass rod compactly. The upper half of the column was bufferized to pH 5.5 and the lower half to pH 6.4. Samples were charged on the column and developed with the upper layer of the solvent mixture of pH 5.5. DNP-Gly, DNP-Gly-Gly and DNP-Gly-Gly-Gly were separated each other forming sharp bands. The bands corresponding to DNP-Gly-Gly and DNP-Gly-Gly-Gly were cut off and eluted with ethanol acidified by small quantity of hydrochloric acid. The eluates were dried up and dissolved in 1% sodium bicarbonate. The optical densities were measured photometrically. After measurement, such DNP-peptides were hydrolyzed with 6N hydrochloric acid for 5 hr. and DNP-derivative was removed by ethylacetate extraction. Aqueous layer was redinitrophenylated, extracted again with ethylacetate, separated by column chromatography and the quantity of DNP-Gly was measured. If the molecular extinction coefficients of dinitrophenyl

9) G. L. Mills, *Biochem. J.*, **50**, 707 (1952).

10) J. L. Perrone, *Nature*, **167**, 513 (1951).

amino acid and peptide are the same, the ratio of optical density of DNP-derivative before and after acid hydrolysis must indicate the length of the peptide. These ratios were 1:1.07 and 1:2.23 respectively for the two DNP-peptides, and were agreed with the expected value for DNP-Gly-Gly and DNP-Gly-Gly-Gly.

Residual aqueous layer (R) in Fig. 2, the yellow color of which shows the presence of unextracted DNP-derivatives, was hydrolyzed with 1 N hydrochloric acid at 100°C for 2 hr. By the same procedure for DNP-peptides, newly formed extractable DNP-derivatives were taken into ethylacetate-*n*-butanol layer. From this fraction, also, DNP-Gly-Gly and DNP-Gly-Gly-Gly were obtained. This fact shows that the extracts (KA and KB) might contain the longer glycyl peptide. From the procedures described above it was found that the reaction products contain many non-peptide compouds, for example, on the celite column chromatography there appeared DNP-derivatives which have an absorption maximum at 365~380 mμ and do not yield DNP-Gly by hydrolysis. Further, the first extracted solution of reaction product (KA) produces a black colloidal substance on standing at room temperature for 24 hr., and this substance precipitates on acidification.

In order to study the possibility that the polymerized substance remains in the residue as an adsorbed form, determination of nitrogen content of the residue and estimation of mean chain length of peptides were tried using micro-Kjeldahl method and dinitrophenylation technique. Nitrogen distribution in the process of reaction and extraction was shown in Table I. From these data obtained it seems reasonable to assume that not only the expected reaction, i. e., polymerization of aminoacetonitrile, but also the

Table I. Nitrogen distribution in the process of reaction and extraction

	mg. N	%
Starting material	540	100
After reaction period	376	70
Extract (KA)	149	28
Residue (KP)	29	5.3

reaction liberating nitrogen as ammonia or volatile form may take place. Nitrogen content of the residue was lower than expected, but this value varied from one reaction to another between 4~20 per cent. In order to determine the mean chain length of adsorbed polymer, the same procedure as used in the confirmation of two bands on the celite chromatogram was applied to the residue (KP) after refluxing at pH 1 for one hour.

The result of this experiment shows that the mean chain length of adsorbed substance is 1.8. However, it is hard to say that the reaction product involves long-chain, high molecular polyglycine although the residue might adsorb still low molecular peptide and contain the not-straight chain compound as diketopiperazine which produces DNP-Gly by hydrolysis and dinitrophenylation.

The presence of diketopiperazine in the reaction product was supposed by the qualitative test using picrate[11] and the different content of diglycine of the solution with and without alkaline treatment of the hot water extract of reaction product.

Change of Condition.—If the presence of the clay such as kaolin is advantageous for the proposed reaction, one of the effects must be the adsorption of starting material. The degree of adsorption of aminoacetonitrile on several kinds of clay was determined by the following way. The solution of 200 mg. of aminoacetonitrile sulfate in 4 ml. of water was mixed with 1 g. of clay; after shaking the suspension was allowed to stand overnight at 5°C and filtered. The concentration of free aminoacetonitrile in the filtrate and the control solution (without clay) was measured by ninhydrin reaction[12], which is used generally for the determination of amino acid. By a preliminary test it was confirmed that the aminoacetonitrile was not hydrolyzed in the process of determination and could be determined quantitatively, though the color yield is very low. As shown in Table II, the nitrile was adsorbed most

Table II. The degree of adsorption of aminoacetonitrile on the clay

A. pH 4.5

	Adsorption %
Control	0
Kaolin	3.7
Silicic acid	0
Bentonite	27.0
Silica gel	1.0
Japanese acid clay	37.8

B. Adsorption of Japanese acid clay at different pH

pH	Adsorption %	pH	Adsorption %
4.6	37.8	6.8	54.0
4.6	40.0	7.5	45.0
5.5	51.4	8.7	36.5

on Japanese acid clay and at pH 7. This pH coincides with that of the solution of aminoacetonitrile sulfate neutralized with sodium hydroxide solution.

In an effort to study the effect of adsorption on the reactivity, aminoacetonitrile in an adsorbed state was used as starting material. After adsorption, as described above, Japanese acid clay was filtered, dried and heated at 130°C for 3 hr. in the same way as the typical method. In this case, yield of peptides was slightly high, but black colloidal material was produced abundantly at the same time. It may be concluded from the above fact that the adsorption on the clay

11) M. Frankel and E. Katchalski, *J. Am. Chem. Soc.*, **64**, 2264 (1942).

12) S. Moore and W. H. Stein, *J. Biol. Chem.*, **176**, 367 (1948).

activates the starting material to some extent but the effect is not specific for peptide synthesis.

When bentonite, silicic acid, silica gel and alumina were used as adsorbent, the yields of peptides were poor. Kaolin and Japanese acid clay treated with concentrated hydrochloric acid did not adsorb the aminoacetonitrile.

The effect of temperature was investigated between 100~150°C; below 120°C the reaction did not occur, and above 150°C the decomposition was predominant.

When methylene aminoacetonitrile was used instead of aminoacetonitrile as starting material, many spots appeared on the paper chromatograms of the extract of reaction product, but Gly-Gly-Gly could not be detected. In this case, the extracted solution (corresponding to KA) gave positive biuret reaction, but since several positive compounds besides poly-peptide have been known, biuret test is not suitable to such solutions which involve various unknown substances similarly as the test of diketopiperazine by picrate.

As cited in the introduction of this paper, diaminopyrimidine was synthesized from thiourea and malonitrile in ethanol in the presence of sodium ethoxide by Traube. If aminoacetonitrile reacts analogously, diimino-piperazine may be obtained from two molecules of aminoacetonitrile to yield diketopiperazine and diglycine by hydrolysis.

Four grams of aminoacetonitrile sulfate was suspended in 10 ml. of ethanol. To this suspension, 20 ml. of ethanol dissolving 1.4 g. of sodium was allowed to run from a dropping funnel under stirring. Two aliquots of the mixture were heated to 40°C and to boiling point, respectively, for 3 hr. In each case, the product was neutralized, dried in vacuo, and dissolved in 1 N sodium hydroxide. After 1 hr. the product was neutralized again, dried and subjected to paper chromatography. Only a trace of glycyl-glycine was observed, and here again the black colloidal substance appeared in the solution of the product.

Discussion

As aminoacetonitrile has a bifunctional group and an active methylene group, it may be reactive and be able to cause various reactions simultaneously. These characteristics are a strong point as well as a weak point in the case of polymerization which was tried. From the result of investigation, it was obvious that peptides were formed from aminoacetonitrile, but the presence of high polymer which might be firmly adsorbed on the clay was not confirmed. If the conditions may be found, in which polypeptide synthsis is promoted while the side reaction and decomposition are suppressed, poly-glycine should be yielded more easily. Because the heat reaction of aminoacetonitrile without clay was unsuccessful, the solid surface of clay seems to play a certain role in this reaction as in the case of activation of the methylene group of polyglycine[6].

In some cases, the formation of only glycyl-glycine was observed in the typical reaction procedure. Though it is hard to explain, this phenomenon suggests that the reaction proceeds in two directions, the one toward diketopiperazine formation and the other toward polyglycine formation similarly as the polymerization of glycine ethyl ester.

Summary

Aminoacetonitrile sulfate was heated with kaolin and/or Japanese acid clay at 120~140°C for 5 hr. The presence of glycyl-glycine and glycyl-diglycine in the extract and the partial hydrolysate of this reaction product was confirmed by paper and column chromatography.

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Phase Transition of Li_2O-Fe_2O_3 System. III. Long-range Order in Lithium Ferrite and Lithium Ferrospinel

By Eizo KATO*

(Received July 22, 1958)

In the previous papers[1,2], the thermal and the electric properties of lithium ferrite and lithium ferrospinel were studied from the viewpoint of an order-disorder transition. Then the anomalous phenomena in these properties were observed at the transition.

The order-disorder transition in binary alloys has been widely studied by the statistical thermodynamics[3]. In order to specify the degree of order for the arrangement of atoms, two kinds of order parameters are defined. One is a long-range parameter introduced by Bragg and Williams, and the other is a short-range order parameter introduced by Bethe. When the former parameter is present, some super-stucture reflections appear in an X-ray diffraction. At the transition temperature, this parameter vanishes and the latter parameter remains in a diffuse scattering of X-rays.

The long-range order parameter in a substitutional transition, which was defined by Buerger[4], has not yet been measured except of binary alloys. As the first example of an extension of the transition theory for binary alloys to more complex crystals, temperature dependencies of the long-range order parameter for lithium ferrite and lithium ferrospinel were measured by an X-ray powder method.

Diffraction Theory of Long-range Order

The long-range order parameter S may be written as

$$S=(r_\alpha-p_A)/(1-p_A)=(r_\beta-p_B)/(1-p_B) \quad (1)$$

where r_α is the fraction of α site occupied by A ions and p_A is the fraction of A ions in the crystal, and so forth. S is, of course, defined so that it may be unity for the perfectly ordered state and zero for the perfectly disordered one. When the crystal is of AB type or of AB_3 type, S is given from Eq. 1.

$$S=2r_\alpha-1=2r_\beta-1 \quad \text{for AB type} \quad (2a)$$

and

$$S=(4r_\alpha-1)/3=4r_\beta-3 \quad \text{for } AB_3 \text{ type} \quad (2b)$$

Let us consider the order-disorder equilibrium, in which two kinds of ions in the crystal contribute to the transition, i.e.,

$$A_aB_bL_l\cdots\cdots N_n \rightleftarrows (A_aB_b)L_l\cdots\cdots N_n$$

where A_a means that a A ions are at the definite equivalent points, and so forth and (A_aB_b) means that a A ions and b B ions are randomly distributed to the points. According to the method used for binary alloys, the expression for the structure amplitude of any state is

$$F=[f_Ar_\alpha+f_B(1-r_\alpha)]G_\alpha + [f_Br_\beta+f_A(1-r_\beta)]G_\beta+\sum_L F_L \quad (3)$$

where f_A is the atomic scattering factor for A ion, f_B that for B ion, G_α and G_β are the geometrical structure factors referring only to the positions of α site and β site respectively, and $\sum_L F_L$ is the sum of structure amplitudes as to L,……, N ions which are independent of the transition. When A_aB_b is AB or AB_3, Eq. 3 is rewritten by introducing Eq. 2,

$$F=S(f_A-f_B)/2\cdot(G_\alpha-G_\beta) + (f_A+f_B)/2\cdot(G_\alpha+G_\beta)+\sum_L F_L \quad \text{for AB} \quad (4a)$$

and

$$F=S(f_A-f_B)/4\cdot(3G_\alpha-G_\beta) + (f_A+3f_B)/4\cdot(G_\alpha+G_\beta)+\sum_L F_L \quad \text{for } AB_3 \quad (4b)$$

For simplicity, both cases are expressed by a single form as

$$F=SF_{ss}+F_{fund} \quad (5)$$

where the subscript *ss* means the superstructure reflection and *fund* the funda-

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1) E. Kato, This Bulletin, **31**, 108 (1958).

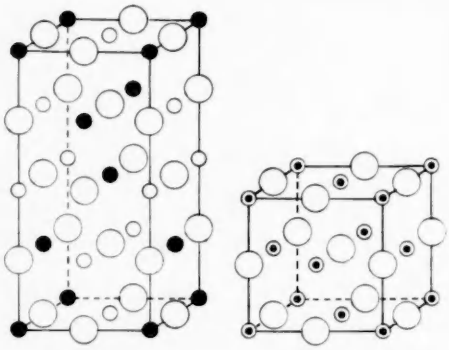
2) E. Kato, ibid., **31**, 113 (1958).

3) See, for instances, S. Siegel, "Phase Transformations in Solids", Wiley, New York (1951), p. 366; T. Muto and Y. Takagi, "Solid State Physics", Vol. 1, Academic Press, London (1955), p. 193.

4) M. J. Buerger, "Phase Transformations in Solids", Wiley, New York (1951), p. 183.

5) Z. W. Wilchinsky, *J. Appl. Phys.*, **15**, 806 (1944); D. T. Keating and B. E. Warren, ibid., **22**, 286 (1952).

mental reflection. SF_{ss} and F_{fund} correspond respectively to the first term and the rest two terms in Eq. 4.



(ordered lattice) (disordered lattice)

Fig. 1. Crystal structures of lithium ferrite.
○ Li^+ ion ● Fe^{3+} ion ○ O^{2-} ion
⊙ $\frac{1}{2}$ ($Li^+ + Fe^{3+}$)

The above-mentioned procedures were applied to the transition between $D_{4h}^{19} - I4_1/amd$ and $O_h^5 - Fm3m$ in lithium ferrite, and to that between $O^6 - P4_332$ and $O_h^7 - Fd3m$ in lithium ferrospinel. The crystal structures of lithium ferrite are shown in Fig. 1, where oxygen ions are at the same equivalent point in either the perfectly ordered or the perfectly disordered state. The crystal structures of lithium ferrospinel are shown in Fig. 2, where the equivalent points of ferric ions (small shaded circles) at the tetrahedral sites of the eightfold position are the same in either state, and the structural parameter of oxygen ions (large circles) is 0.382[6] at the perfectly ordered state and 0.382 ± 0.005[7] at the perfectly disordered state. Under the following postulations,

(1) oxygen ions in lithium ferrite, and oxygen ions and tetrahedrally-coordinated ferric ions in lithium ferrospinel are independent of the transition mechanism,

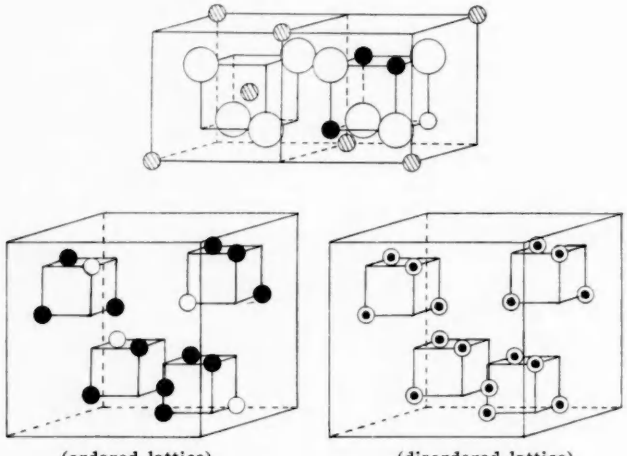
(2) the migrating ions, i.e., all the cations in lithium ferrite or the octahedrally-coordinated cations in lithium ferrospinel, occupy the equivalent points invariable at any state of the transition,

the structure amplitudes of the superstructure reflection can be calculated from Eq. 4 as follows:

For lithium ferrite

$$|F_{ss}| = 2\sqrt{2}\,(f_{Fe} - f_{Li}),\ h+k = 2n+1,\quad l = m+1/2\ (L = 2l = 2m+1) \tag{6a}$$

and for lithium ferrospinel



(ordered lattice) (disordered lattice)

Fig. 2. Crystal structures of lithium ferrospinel. Above: One-fourth of a unit cell of the ordered lattice. Below: Total unit cell showing the tetrahedrons of $LiFe_3$.
◍: Fe^{3+} ion at the tetrahedral site ○: Li^+ ion at the octahedral site
●: Fe^{3+} ion at the octahedral site ⊙: $\frac{1}{4}$ ($Li^+ + 3Fe^{3+}$) ○: O^{2-} ion

6) P. B. Braun, *Nature*, **170**, 1123 (1952).
7) F. de Boer, J. H. van Santen and E. J. W. Verwey, *J. Chem. Phys.*, **18**, 1032 (1950).

$$|F_{ss}| = \begin{cases} 2(f_{Fe}-f_{Li}), & h,k,l: \\ & \text{one even and two odd} \\ 2\sqrt{2}\,(f_{Fe}-f_{Li}), & h,k,l: \\ & \text{one odd, one } 4n, \text{ one } 4m+2 \end{cases} \quad (6b)$$

where f_{Li} is the atomic scattering factor for lithium ion and f_{Fe} that for ferric ion. Here, in lithium ferrite, l indicates the third index of a plane which refers to the cubic unit cell in the perfectly disordered state and L that referred to the tetragonal one in the perfectly ordered state, the latter cell being double of the former along c direction.

Experimental and Results

Specimens.—Lithium ferrite and lithium ferrospinel were prepared by the same method as in the previous papers[1,2]. The probes for X-ray measurements were made by quenching in water after heating for a necessary time at the definite temperatures which were listed in Tables I and II.

TABLE I. ANNEALING TIMES, TEMPERATURE AND VALUES OF S FOR SAMPLES OF LITHIUM FERRITE

Temp. (°C)	Annealing time (days)	Peak area $A_{10\frac{1}{2}}$	Peak area A_{200}	S
518	20	4263	2798	0.92
554	21	4928	3017	0.95
587	28	0	—	0
598	28	0	—	0
616	30	0	—	0
627	27	0	—	0
642	15	0	—	0
650	34	0	—	0
661	11	0	—	0

$A_{10\frac{1}{2}}$ in the range of 616~661°C were measured by the film method.

TABLE II. ANNEALING TIMES, TEMPERATURE AND VALUES OF S FOR SAMPLES OF LITHIUM FERROSPINEL

Temp. (°C)	Annealing time (hr.)	Peak area A_{210}	Peak area A_{220}	S
448	53	636	1831	0.95
542	61	688	1839	0.98
652	60	665	1910	0.95
708	64	635	1805	0.96
721	95	623	1816	0.94
744	140	194	1784	0.53
765	24	0	—	0
802	25	0	—	0

Apparatus.—The X-ray reflection intensity was measured by a Norelco diffractometer with filtered Co K_α radiation.

Procedures.—From the observed integrated intensities of a super-structure reflection and a fundamental reflection, S is computed by the following formula,

$$S^2 = \left(\frac{P_{ss}}{P_{fund}}\right) \frac{F_{fund}^2[m(1+\cos^2 2\theta)\operatorname{cosec}^2\theta\sec\theta]_{fund}}{F_{ss}^2[m(1+\cos^2 2\theta)\operatorname{cosec}^2\theta\sec\theta]_{ss}}$$

where P: integrated intensity
m: multiplicity
θ: Bragg angle of the reflection

since $F_{ss}=0$ on the fundamental reflection and $F_{fund}=0$ on the super-structure reflection. The integrated intensity is proportional to the area A under the peak curve traced by diffractometer for the reflection, i.e.,

$$P_{ss}/P_{fund} = A_{ss}/A_{fund}$$

Lithium Ferrite.—The super-structure line $10\frac{1}{2}$ [8] and the fundamental line 200 were chosen. The final results are listed in Table I.

Lithium Ferrospinel.—The super-structure line 210 and the fundamental line 220 were chosen, and 0.382 was adopted for the value of structural parameter of oxygen ion. The final results are listed in Table II.

Discussion

The statistical theory[9] for the order-disorder transition has been studied on binary alloys. In the simplest case, the approximation is given by Bragg and Williams in which the effect of the nearest neighbors is neglected. Considering the nearest neighbor interaction only, the first approximation is derived from the Bethe's method. Although it may not always be valid to apply the theory for the order-disorder transition in binary alloys to such complex crystals as lithium ferrite and lithium ferrospinel it can be permitted, for the sake of simplicity, to make a trial as follows. Namely, if we neglect the ions which have no direct contribution to the transition, the remaining lattice constructed by the migrating ions alone belongs to the binary system to which the theory may be applied. This lattice is conveniently named a simplified lattice.

The simplified lattice of lithium ferrite belongs to AB type and its disordered lattice is a face-centered cubic. Comparison of the experimental results for lithium ferrite with the curves calculated by the zeroth approximation and the first one for AuCu[10], which is one of binary alloys

8) Here is represented the index of the plane referred to the disordered lattice.

9) See, for instance, E. A. Guggenheim, "Mixtures", Oxford Univ. Press, London (1952), p. 101.

10) The theory gives the following results: from the zeroth approximation $T/T_c = S/\tanh^{-1}S$, where T_c is the transition temperature; from the first approximation in which all combinations of the quadruplets of sites are considered, the value of S jumps from random value zero to the value $S=0.9828$ at T_c[9].

of face-centered cubic type, is shown in Fig. 3[11]. The experimental results are in qualitative agreement with the curve by the first approximation for AuCu. Comparing the crystal structures of the simplified lattice of lithium ferrite with those of AuCu lattice, both lattices have similar structure in disordered phase. The ordered AuCu lattice is pseudo-cubic (tetragonal but the axial ratio is 1.08 : 1.08 : $\sqrt{2}$), while the ordered lattice of lithium ferrite is a tetragonal one which is double the size of cubic lattice in the disordered state along c axis as is seen in Fig. 1. However, the number of the nearest neighbor is 12 in either lattice although the relative arrangement of A and B atoms on these 12 positions around the centered atom is different in both lattices. Hence under such a rough assumption as neglecting oxygen ions as mentioned above, lithium ferrite can be approximated to be LiFe as AuCu with respect to its transition.

On the other hand, the simplified lattice of lithium ferrospinel belongs to AB_3 type, the typical example of which is $AuCu_3$ (face-centered cubic type). Comparison of the experimental results for lithium ferrospinel with the curves calculated by the zeroth and the first approximation for $AuCu_3$[12] is shown in Fig. 4, where it is found that the experimental results are in good agrreement with the curve calculated by the first approximation. It is noted here that the groups of $AuCu_3$ are arranged side by side along the three directions while those of $LiFe_3$ are arranged tetrahedrally as is seen in Fig. 2, as a result of which the number of the first neighbors is 12 in $AuCu_3$ but 6 in $LiFe_3$[13]. In the present stage the effect of the number of the first neighbor is not ascertained.

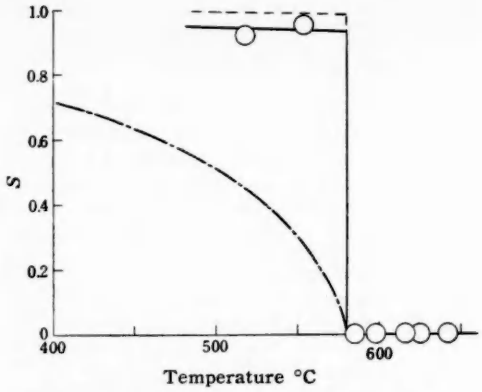


Fig. 3. Variation of long-range parameter for lithium ferrite, experimental and theoretical.
-○-: experimental
- · -: zeroth approximation
------: first approximation

In conclusion, it is very interesting that

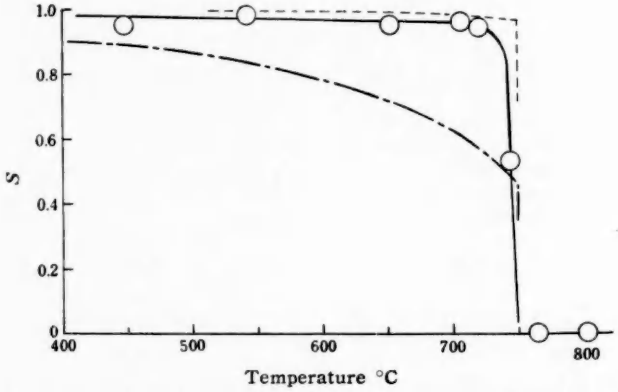


Fig. 4. Variation of long-range order parameter for lithium ferrospinel, experimental and theoretical.
-○-: experimental, - · -: zeroth approximation, ------: first approximation

11) Here T_c is conveniently assumed to be 580°C.

12) The theory gives the following results: from the zeroth aproximation $T/T_c = \frac{4.88\,S}{\ln\{1+16S/3(1-S)^2\}}$; from the first approximation in which all combinations of the quadruplets of sites are considered, the value of S jumps from the random value zero to the value $S=0.9557$ at T_c[9].

13) It may be shown that T_c can not exist in the case of six nearest neighbors (private communication from R. Fujishiro).

in spite of such a rough assumption as ignoring serveral ions having no direct contribution to the transition, statistical theory for order-disorder transition in binary alloys can be approximately applied to estimation of the long-range order parameter in such complex crystals as lithium ferrite and lithium ferrospinel. Moreover, it is emphasized that in the present stage where we have no theory including the effect of all ions in the complex crystal, the assumption of the simplified lattice which can reduce the complex system to a binary one is very useful in treating the order-disorder phenomena.

Transition Temperature of Lithium Ferrite.—As is shown in Fig. 3 the long-range order in lithium ferrite vanishes at 554~587°C[14]. In the previous paper[1] it was found that the anomalous thermal expansion took place at 660°C in the case of ascending temperature and no change was measured down to 550°C in the case of descending temperature. In both the differential thermal analysis and the electric measurement a change was recognized in the vicinity of 660°C. This discrepancy between the observed transition temperatures by X-ray method and those by others is due to the fact that the samples used in the X-ray method were annealed for a long time (20~30 days), while the dilatometry was measured under the non-equilibrium condition, because of its sluggish transition.

Transition Temperature of Lithium Ferrospinel.—The value of the transition temperature for lithium ferrospinel was decided to be 750±1°C from the dilatometry. This value was also given from the differential thermal analysis and the measurement of d.c. electric resistance. The diffractometric curves used for the determination of the transition temperature are shown in Fig. 5, where the superstructure lines 210 and 211 are as yet prominent at 744°C, but very faint at 747°C and disappear completely at 756°C. Hence the probable value of the transition temperature can be estimated to be 750°C in good agreement with the value determined by other physical methods.

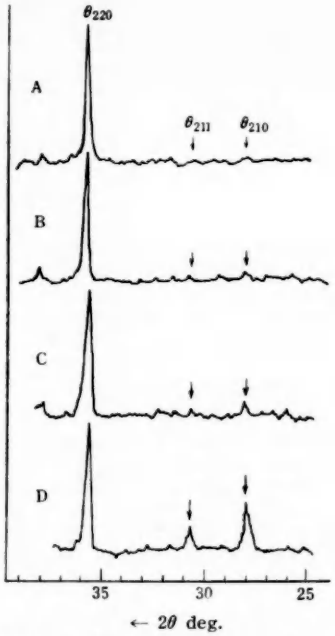


Fig. 5. Diffractometric curves for some samples of lithium ferrospinel in the neighborhood of the transition temperature.
A: 756°C, B: 747°C, C: 744°C, D: 721°C

The author wishes to express his appreciation to Professor S. Nagaura for his encouragement during this work. He is also indebted to Professor R. Fujishiro for his kind instruction on the statistical treatment and to Professor Y. Saito for his suggestion on X-ray diffraction theory.

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14) By R. Collongues (*Bull. soc. chim. France*, **1957**, 261) the ordered phase was found at 600°C for a sample annealed for 25 days.

*Preparation of Chloropolysilane from the Copper-catalyzed Reaction of Silicon Metal and Hydrogen Chloride**

By Isao SHIIHARA and Jun IYODA

(Received November 13, 1958)

The copper-catalyzed reaction of silicon metal powder with hydrogen chloride by the flow method was studied in order to find a convenient preparative method for chloropolysilanes, and to elucidate the mechanism of this reaction which seems to have a close relationship with the so-called direct method of preparing alkylchlorosilanes. Hitherto, the conventional way to prepare chloropolysilanes has been to use a binary alloy such as magnesium-silicon[1,2] or ferrosilicon[1] so as to smooth the reaction of silicon and chlorine, and to work at a temperature as low as possible. However, the yields were not satisfactory.

The present investigation was carried out with several kinds of silicon-copper powder mixtures, varying the species of silicon metal, the reaction temperature, the flow velocity of reactant gas, and the ratio of copper powder to silicon. Under the optimum conditions, the yield of chloropolysilane was found to reach 30 wt. % based on the amount of hydrogen chloride. The preferable species of metallic silicon were those which contained aluminum as a main impurity.

Experimental

Materials. — *Metallic silicon of commercial grade.*—Three species of metallic silicon which contained aluminum (Samples A and C) and iron (Sample B), respectively, as main impurities were used in these experiments after being crushed and pulverized into minus 80 mesh. The analytical values of each sample were as follows:

Sample	Exptl. run No.	Fe%	Al%	Ca and Mg%	Particle size (mesh)
A	1, 4, 5, 7	2.70	1.60	0.2	80～150
B	2, 3	7.94	0.42	—	80～120
C[3]	6, 8	trace	0.52	—	120～170

Silicon-aluminum and silicon-calcium alloys. — An alloy having the composition Si:Al=8:2 was prepared by melting 98% silicon and aluminum block in a sealed graphite crucible. Another was a commercial silicon-calcium alloy. Both were crushed and pulverized into minus 80 mesh. The analytical values of the two alloys were as follows:

Sample	Si%	Al%	Fe%	Cu%	Ca%	Particle size (mesh)
Si-Al alloy	80.6	17.2	1.02	0.01	—	80～120
Si-Ca alloy	27.3	—	—	—	68.6	80～120

Copper powder.—Finely pulverized copper for catalyst, prepared by the Fukuda Metal Plate and Powder Mfg. Co., and known as "3L3" (Purity: >98%; size minus 200 mesh[4]), was used.

Hydrogen chloride. — It was prepared in the usual way by the reaction of ammonium chloride and sulfuric acid, washed and dried by concentrated sulfuric acid, and reserved in a 20 l. glass bottle tank which was sealed by concentrated sulfuric acid. The gas was made to flow by the pressure of the sealed liquid head and was measured by its volume (Fig. 1).

Apparatus and Experimental Procedure.— The whole apparatus is shown in Fig. 1. About 20～200 g. of contact mass was charged into a reaction tube of 3 cm. diameter and 1 m. length in an electric furnace. After replacing the air in the apparatus with nitrogen, it was heated to about 150°C in order to dry off the absorbed water and cooled. Then the temperature was raised again from room temperature at the rate of 4～5°C/min. while passing hydrogen chloride at the rate of 8 l./hr. The initiation of the reaction was observed by sudden rise of temperature, change in volume of evolved hydrogen gas, and fuming in the adapter part which was due to the generation of aluminum chloride or chlorosilanes. As explained in our former report[5], the temperature at which this initiation occurred was designated as initiation temperature, or I.T. as abbreviated. Once the reaction occurred, the contact mass was activated and thus the succeeding reaction could proceed at a somewhat lower temperature. Accordingly the reaction tube was cooled to room temperature and then re-heated gradually in order to determine the actual

* Presented before the Symposium on the organosilicon and organometallic compounds held at Osaka under auspices of Kinki Chemical Industries Association, Oct. 15, 1957.

1) W. C. Schumb and E. L. Gamble, "Inorganic Synthesis", (H. S. Booth, Editor in Chief), McGraw-Hill Book Co., Inc., New York (1939), p. 42.

2) W. L. Walton, U. S. Pat. 2,602,728 (1952).

3) A powder of silicon-aluminum alloy was treated with dilute hydrochloric acid and washed with water and dried.

4) −200～+250 mesh 9%; −250～+325 mesh 15%, −325 mesh 76%; covering power 1900 cm^2/g.

5) I. Shiihara and J. Iyoda, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **60**, 1388 (1957).

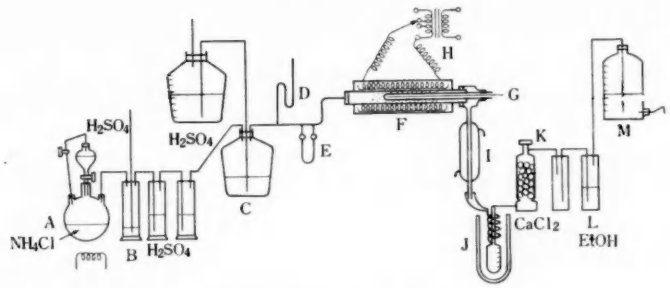


Fig. 1. Reaction apparatus for Si(Cu)+HCl gas.
A: HCl generator B: Drying bottle and prevention of backflow
C: Storage and measuring bottle of HCl gas D: Manometer
E: Flowmeter F: Reaction tube and electric furnace
G: Thermocouple H: Transformer I: Water condenser
J: Dry Ice condenser K: Prevention of moisture and backflow
L: Absorption bottle of HCl M: Mariotte bottle.

starting point of reaction, or R.T. as abbreviated. After the confirmation of R.T., the reaction was carried out by making hydrogen chloride flow under the appropriate conditions. The condensates, both in the water-cooled receiver and in the Dry Ice trap, were combined and distilled through a Widmer column and separated into trichlorosilane, silicon tetrachloride and residue with a high boiling point. The residual contact masses were analyzed by the usual methods as to metallic silicon, volatile silicon component on treating with hydrofluoric acid, copper and chlorine. In each experiment, the unreacted hydrogen chloride and volatile chlorosilane in the effluent gas were absorbed in ethanol and the amount of acidic chlorine was measured by titration and silica by weight. Thus insoluble gas was accumulated as hydrogen in a Mariotte bottle and measured.

Results

Effect of the Other Metallic Ingredients in Silicon Metal.—In our previous experiments it was found that the species of silicon metal have a direct influence upon the so-called direct method of preparing methylchlorosilanes. Accordingly, in order to investigate the effect of ingredients in silicon metal, three representative species of silicon metal powder (Samples A, B and C) and silicon-calcium were chosen as contact masses in the present experiments. Because of the prominent catalytic action of copper in the reactions, experiments were conducted with special addition of 3 wt. % copper powder with three kinds of silicon metals. In the case of chips of silicon-calcium alloy no catalyst was used because of the great reactivity of the alloy at lower temperatures, i.e., about 150°C.

A summary of experimental results is shown in Table I. It was found that Sample A—fairly rich in aluminum ingredient—was the best contact mass among the four species tested, and showed its optimum temperature of 215°C for forming the best yield of chloropolysilanes. In silicon-calcium, the product was found to be almost exclusively chloromonosilane, although the R.T. was as low as 150°C.

Influence of Elapse of Reaction Time.—It was found that with long reaction runs the yield of chloropolysilane gradually increased as the reaction time increased. An example with the silicon Sample A is shown in Table III.

The flow rate of hydrogen chloride in the run was almost equal from beginning to end, i.e., 8 l./hr. It seems that the higher molecular weight polysilane derivatives which were produced on the contact mass as intermediates would increase as the elapse of reaction time, just as it will be shown in the case of the contact mass of high copper ratio. From these intermediates some lower series of chloropolysilanes, such as di- or trisilane, might be split out.

Effect of the Copper Catalyst.—As was known in many previous experiments, the reaction of silicon metal or silicon alloy with hydrogen chloride was promoted when a small per cent of copper was added as catalyst.

Copper enables this reaction to proceed even at 215°C; without the copper catalyst

TABLE I. EFFECT OF THE OTHER METALLIC INGREDIENTS IN SILICON METAL

Contact masses	Run No.	Reacn. temp.	Reacn. time	HCl used	Liquid product	Yield	Absorption in EtOH		Distillation analysis				
							HCl	SiO_2	H_2SiCl_2	$HSiCl_3$	$SiCl_4$	High b.p. materials	Loss
		(°C)	(hr.)	(g.)	(g.)	(%)	(g.)	(g.)	(%)	(%)	(%)	(%)	(%)
Si (A) (Al rich)	H-1-(10)	215	6	85.2	102	119	7.55	0.1	0	35.5	24.0	37.5	3
200 g.	H-4-(4)	170	6	79.6	42	52.7	35.6	2.0	0	58.5	13.6	23.4	4.5
Cu 6 g.	H-4-(6)	275	6	90.0	107.5	111	4.25	1.7	0	65.7	21.9	8.6	3.8
	H-4-(9)	180	6.5	86.1	56	65.0	35.0	2.8	0	86.5	13.4	26.8	3.4
Si (B) (Fe rich)	H-2-(4)	215	6	97.3	93	95.7	20.4	1.1	0	57.3	18.3	23.1	1.3
200 g.	H-2-(8)	355	6	92.0	78.5	85.2	29.8	0.7	0	63.2	25.7	8.7	2.4
Cu 6 g.	H-3-(6)	275	7	107	131	112	1.2	0.3	0	60.8	23.2	12.7	3.3
Si (C) (HCl aq. treated) 107 g. Cu 3.3 g.	H-8	275	5	111.8	97	86.8	27.0	0.5	5.8	65.6	13.2	12.2	3.2
Si—Ca* 1.1 kg.	previously performed	150	6.5	144.2	87	61.2	—	—	0	41.7	52.5	2.8	3.0

* 2~3 mm. chip was used.

TABLE II. THE EFFECT OF ADDITION RATIO OF COPPER CATALYST TO SILICON METAL

Contact mass	Run No.	Cu added ratio	Reacn. temp.	Reacn. time	HCl used	Liquid product	Yield	Absorption in EtOH		Distillation analysis			
								HCl	SiO_2	$HSiCl_3$	$SiCl_4$	High b.p. materials	Loss
		(%)	(°C)	(hr.)	(g.)	(g.)	(%)	(g.)	(g.)	(%)	(%)	(%)	(%)
	H-1-1	3	300	3	40.2	43.5	10.8	1.34	0.11	40.4	28.7	25.6	5.3
	H-4-7	3	270	6	86.5	100.5	115.5	4.1	2.3	66.3	20.1	6.5	7.1
	H-4-4	3	215	5	71.4	59	82.6	15.6	3.5	33.9	21.9	36.5	5.9
Si (A)	H-7-5	10	300	2.5	53.6	8	15	40.0	9.8	(10.9 g.)*			
	H-7-4	10	215	2	33.4	3.5	11	39.0	4.4	(4.9)*			
	H-5-2	20	300	2	65.5	61	93.1	20.4	2.7	37.7	26.4	6.6	34.3
	H-5-6	20	215	2.3	40.3	1	2.5	34.9	11.8	(13.2)*			

* As H_3SiCl calculated from absorbed SiO_2 in ethanol (g.).

TABLE III. THE INFLUENCE OF ELAPSE OF REACTION TIME

Contact mass	Cu added ratio	Time elaspe	Reacn. temp.	Reacn. time	HCl	Liquid product	Yield	Absorption in EtOH		Distillation analysis			
								HCl	SiO_2	$HSiCl_3$	$SiCl_4$	High b.p. materials	Loss
	(%)	(hr.)	(°C)	(hr.)	(g.)	(g.)	(%)	(g.)	(g.)	(%)	(%)	(%)	(%)
Si (A)	3	12	215	3	55.4	57	103	10.2	0.05	47.7	16.5	29.4	6.4
		22	215	6	45.6	58	127	7.5	0.07	35.5	24	37.5	3
		34	215	6	92.5	94	102	19.1	2.4	34.6	22.7	40.0	2.7

TABLE IV. i. YIELDS OF CHLOROPOLYSILANE AND DISTILLATION ANALYSIS OF THEM

Contact masses	Run No.	Mean reacn. temp.	Reacn. time	HCl used	Liquid product	Yield (HCl based)	Chloropoly-silane		Distillate to b.p. 180°C (disilane fracn.)		Residual liq. (trisilane fracn.)		Loss
		(°C)	(hr.)	(g.)	(g.)	(%)	(g.)	(%)	(g.)	(%)	(g.)	(%)	(%)
Si (A)	H-1	210	69.3	1053	860	82	248	28.8	202	81.5	42.7	17.2	1.3
Si (A)	H-4	210	68.2	937.4	783	83.4	181.5	23.2	154	85.0	25.5	14.1	0.9
Si (B)	H-2	210	60.0	933.8	813.5	87	150	18.5	123	82.2	25.0	16.1	1.7
Si (B)	H-3	210	47.1	697.5	767	110	62	8.1	52	83.9	8.9	14.3	1.8

ii. REDISTILLATION OF DISILANE FRACTION

Charge: H-1 168.5 g.						
B.p. (°C)	~75	120~143	143~148	148~149	Residue	Loss
Fracn. %	8.6	12.7	5.3	65.1	5.9	1.5
Cl %		80.5		80.0		
Charge: H-4 101 g.						
Fracn. %	7.0	19	12	46	16	0

iii. REDISTILLATION OF TRISILANE FRACTION[a)]

Charge: 86 g.					
B.p. (°C)	~145	145~190	213~215	215~115[b)]	gel residue
Fracn. %	10.5	2.6	35.5	32.5	19.7
Cl %	78.3				

a) The fact that the total sum of this distillation fraction and residue was over 100% and other distillation losses of chloropolysilane were very small, was reasonably explained by the ease of oxidation of chloropolysilane.

b) Violent thermocracking was occurred.

TABLE V. PHYSICAL CONSTANT OF SOME CHLOROMONOSILANES AND CHLOROPOLYSILANES

	Compound	Formula	Mol. wt.	B.p. (°C)	M.p. (°C)	D_{20}^{10}	Cl%
Monosilanes	Silicon tetrachloride	$SiCl_4$	170.0	57.5	−70	1.48	83.5
	Silicochloroform	$HSiCl_3$	135.5	31.5	−128.2	1.34	78.5
	Dichloromonosilane	H_2SiCl_2	102.1	8.0		—	69.6
Disilanes	Hexachlorodisilane	Si_2Cl_6	269.2	149	2.5	1.47	79.3
	Pentachlorodisilane	HSi_2Cl_5	234.5	125			75.6
Trisilanes	Octachlorotrisilane	Si_3Cl_8	367.9	215	−67	1.56	77.1
	Heptachlorotrisilane	HSi_3Cl_7	333.5	unknown		—	74.4

TABLE VI. REACTION OF THE CHLOROPOLYSILANES $H_nSi_mCl_{2m+2-n}$ AND COPPER POWDER

Expt. No.	Samples of chloro-polysilanes	(g.)	Catalyst	(g.)	H_2 generated (cc.)	Reacn. time (min.)
1		3.729	Cu powd.	0.5	2.8	20
2	Disilane fracn.	2.440	Cu+$AlCl_3$	0.5+0.5	16.9	10
3	B.p. 120~143°C in Table IV	2.570	CuCl	0.5	0	10
4		2.570	CuCl+$AlCl_3$	0.5+0.5	0.4	10
5		6.859	HCl+$AlCl_3$	0.5	ca. 60	15
6	Si_2Cl_6 b.p. 143~148°C	15.0	Cu+$AlCl_3$	0.5+0.5	4.0	10
7	H-3 residual contact mass	5.0	Cu+$AlCl_3$	0.5+0.5	7.4	10

TABLE VII. ANALYTICAL RESULTS OF THE RESIDUAL MASSES IN EACH RUN

Run No.	H-1	H-2	H-3	H-4	H-5-2	H-5-6
Residual wt.(g.)	33	60	43	35.08	116	55[a]
Si species	A	B	B	A	A	A
Ignition loss (%)	46.97	48.43	2.19	35.40	−3.50[b]	−6.74[b]
SiO_2[c] (%)	16.10	12.43	29.83	57.11	7.43	6.61
Si (%)	6.91	4.10	23.88	0	62.82	56.48
Fe (%)	11.76	18.33	26.67	11.42	2.35	4.24
(Recovery)[d] (%)	(71.7)	(69.7)	(72.8)	(74.2)	(100)	(86.4)
Cu (%)	15.21	7.18	11.14	18.05	19.75	24.20
(Recovery)[d] (%)	(83.7)	(71.8)	(80.2)	(106.0)	(95.4)	(93.8)
Cl (%)	34.62	37.10	2.19	3.69	1.74	0.55
Total (%)	84.60	79.14	93.71	90.27	94.09	92.08

a) 37 g. was sampling out at intervals.
b) When the content of chlorine and volatile silicon hydrides in contact masses was small, this value often became a negative value because of the increase of weight caused perhaps by oxydation of the contact mass in air.
c) This value was calculated so as to take the weight difference after and before the treatment of HF solution as silica, but presumable some Si—Cl and Si—H might be remained even if they were ignited in air.
d) % of recovery to the starting contact masses.

it was necessary to raise the temperature to 300°C[6] in order to get a sufficient yield of liquid product. This effect makes it possible to get chloropolysilane and siliconhydrides in more satisfactory yield, which are both unstable at temperatures higher than 250°C, the temperature used in the hitherto-performed procedures.

As to the amount of the copper added to the silicon metal, it was remarkable that it showed optimum at 1~3 wt. % copper content, and the increased ratios of copper, for instance 10% or 20%, yielded less liquid chlorosilane (Table II). This was due to the formation of monochloromonosilane which could not be condensed in a Dry Ice-acetone trap but was absorbed in alcohol. The reason for the formation of a small amount of chloropolysilanes may be the smaller reactivity of some higher molecular weight cupropolysilanes which might be formed by the reaction of Eq. E proposed in the discussion part of this report. These compounds

6) F. C. Whitmore, *J. Am. Chem. Soc.*, **69**, 2108 (1947).

might be produced proportionally to the amount of copper, and would not be able to accept further cleavage reaction of hydrogen chloride and remained as solid materials on contact mass. Moreover, the life of contact mass was defined as the interval of the time in which the contact mass is active and forms the liquid product; then the life of the contact mass having a large amount of copper was very short. For instance, 10% and 20% copper masses, have lives of 6.9 and 7.8 hr. respectively as compared to the longer time of 3% copper (Table IV).

Composition of the Chloropolysilanes Condensates.—The contact masses have their own lives and lose their reactivity toward hydrogen chloride at the step where a considerably large amount of silicon component still remains in the residual contact masses (see Table VII). The total figures of a few runs are shown in Table IV. The mean yield of the liquid product was 800 g. from 200 g. silicon metals, and the yields of chloropolysilanes were found to be 8.1~28.8 wt. % as the high boiling residue in the crude product. Distillation analysis was carried out for several intervals of the run in order to investigate the change of the compositions of the crude chlorosilanes with elapse of reaction time (see Table III); however, the distillation of a high boiling point fraction was performed with the gathered sample of several runs. The physical constants of some chlorosilanes and chloropolysilanes of this experiment are shown in Table V. Upon distillation of these chloropolysilanes, the chlorodisilane fraction was found to be 80~85 wt. % and the higher fraction, chlorotrisilane, was found to be 14~17 wt. % based on the charged crude chloropolysilanes. The fraction of trisilane was found to be accompanied by some iron compound, and darkened after some elapse of time. This impurity finally deposited as a brown coagulate of ferric oxychloride, and the upper trisilane distillate became a colorless, transparent liquid. The residual gel substance which was obtained after distilling trisilane was brownish black, generated some hydrogen by hydrolysis in water, violently evolved hydrogen by cleavage in alkaline solution, burned in air with a red flame, and left white ashes. This must have been impure higher chloropolysilanes and did not contain any copper component although it had silicon, iron, aluminum and chlorine in it.

Naturally, it was expected that these chloropolysilanes would possibly have silicon hydride bonds in their molecules arising from the hydrogen atom of hydrogen chloride, contrary to the hitherto-used preparative methods in which chlorine and silicon alloys were used as starting materials. Among the series of $H_nSi_m \cdot Cl_{2m+2-n}$[7], both pentachlorodisilane HSi_2Cl_5 and heptachlorotrisilane HSi_3Cl_7, which were expected to be formed but unknown in literature, were found only in traces in the produced chloropolysilanes and moreover, judging from its boiling point and its hydrogen analysis (Table VI), it was found that the chlorodisilane fraction was rather pure hexachlorodisilane and the chlorotrisilane fraction was also octachlorotrisilane.

As to the hydrogen analysis of the chloropolysilane, there has been no adequate method hitherto[8], but the authors have found that silicon hydride bonds are reactive with metallic copper, especially in the presence of small amounts of anhydrous aluminum chloride when their reactions are carried out in liquid phase.

Therefore, this analysis was performed by the apparatus shown in Fig. 2 in which the polysilanes containing hydrogen were treated with copper powder and $AlCl_3$ in

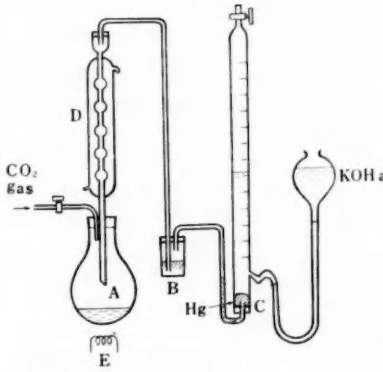


Fig. 2. Apparatus for analysis of Si-H containing chloropolysilane.
A: Reaction bottle
B: Washing bottle with C_2H_5OH
C: Gas burette with KOH aq. and Hg
D: Reflux condenser
E: Heater

7) R. Schwarz, *Z. anorg. u. allgem. Chem.*, **235**, 247 (1938).

8) V. G. Fritz, ibid., **280**, 135 (1955).

a bottle A. The method devised was almost analogous to that of Dumas' nitrogen analysis, i.e., the evolved hydrogen was carried by carbon dioxide and the hydrogen produced gathered in a gas burette on potassium hydroxide solution and measured. The results of this hydrogen analysis are shown in Table VI. This method was confirmed previously with the known silicon-hydride containing substance, for instance, with Ph_3SiH, and showed a fairly good agreement. The occurrence of silicon-copper bond which was made by the reaction of silicon hydride and copper may be recognized by the change of metallic copper to gray metallic silicon color. It was also known that the liberated gas was hydrogen. The contents of silicon hydride in these chloropolysilanes were proved to be very small according to this analysis.

One must be careful in treating chloropolysilanes, because they are apt to form certain dangerous materials. When hydrolyzed in air, they form compounds which exqlode with slight friction or shock. These chloropolysilanes have a flammable nature although they consist only of silicon and chlorine.

Composition of the Residual Reaction Mass.—The final residual masses which were left after reaction had an appearance of very voluminous light powder possessing no metallic lustre like starting silicon, and were caqable of burning in air when ignited, revealing a very brilliant blue flame by burner test.

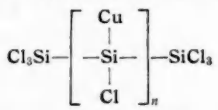
The results of chemical analysis are shown in Table VII. The amounts of hydrogen evolved on treating the residues with alkali solution are given in Table VIII.

TABLE VIII. HYDROGEN GENERATION ON TREATING THE RESIDUAL MASSES WITH 10% SODIUM HYDROXIDE SOLUTION

Sample	(g.)	H_2 evolved (m mol./g.)	SiO_2 (g.)	Si%	H/Si atom ratio
H-2	0.1240	2.00	0.0114	4.30	2.61
H-2	0.1280	1.85	0.0160	5.65	1.78
H-3	0.1330	5.75	0.0412	14.50	2.23
H-3	0.0950	5.34	0.0351	17.20	1.74
H-4	0.1570	3.20	0.0461	13.70	1.31

These facts led to the conclusion that the remainder may be the higher molecular weight chloropolysilanes and that some chloropolysilanes, especially those which have much silicon-copper bond in them, could not be cleaved by hydrogen chloride even if the copper catalyst were present, and so the reaction ceased.

If it was supposed that all iron was converted into ferrous chloride and copper remained as metal[9], the residual number of chlorine atoms of the final contact masses in H-1 and H-2 would be almost equal to the number of the silicon atoms, and the hydrogen atoms generated by alkali solution would be also twice as much as the silicon atoms (Table VIII). As the final reaction temperature, rather high temperatures, say 475°C for H-1, 460°C for H-2, were applied, and so it may be reasonably considered that all the iron changed to ferrous chloride, and in the final stage of this reaction almost every silicon atom has one chlorine atom linked to it, and the silicon atoms are linked to each other with silicon-silicon bonds. Thus, the proposed structure of these chloropolysilanes is as follows:



However, the contact mass in the reaction course was thought to contain much more silicon hydride bond than the final structure proposed above, because samples H-3 and H-5 in the reaction were of a more flammable nature than that of H-1, H-2 and H-4 of the final stages. The amount of silicon hydride bond in the former contact masses was measured by the generation of hydrogen with copper and aluminum chloride and found to be high (Table VI).

I. T. and R. T. Measurements.—Many I. T. and R. T. measurements were performed at the beginning of each run and with the special contact mass species. The results of observations are listed in Table IX, and also some examples of the graph with I. T. and R. T. measurements are shown in Fig. 3. The sudden rise in the temperature curve in comparison with the blank curve[10] showed the occurrence

9) The forms of iron and copper componet were found by extracting H-1, H-2 residual contact masses with dimethylformamide. Their salts are both soluble in this solvent, but the extracted ones were almost ferrous chloride and not cuprous chloride.

10) The blank curves were figured separately by measuring temperature versus time at several voltages in an electric furnace. Nitrogen gas was passed at the rate of 8 l./hr. (the same as that of hydrogen chloride) into the reaction tube containing the same amount of contact mass as in the actual measurements. This was repeated several times and each time the same curve was obtained. Thus, this curve could be considered as a blank.

○ Temperature (°C)

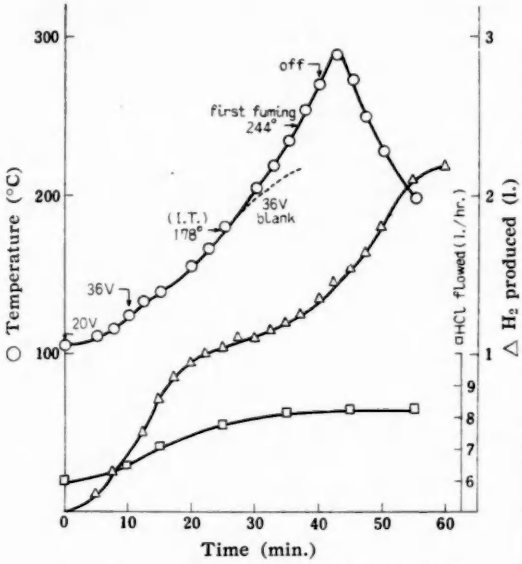


Fig. 3a. An example of the graph with I.T. measurement (H-3-1).

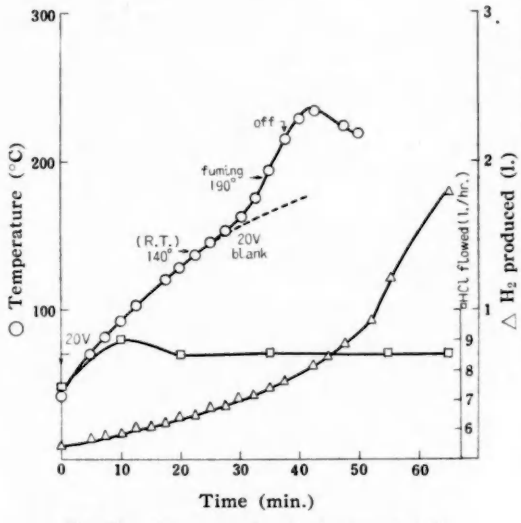


Fig. 3b. An example of the graph with R.T. measurement (H-3-2).

of the reaction about the contact mass. At this critical point, usually some gas evolution, or rate change of gas generation, or fuming caused by the product in the adaptor part were also present, and these could be also considered the evidence of the reaction occurrence, but these

TABLE IX. I.T. AND R.T. OF THE REACTION OF SOME SILICON CONTACT MASSES WITH HCl UNDER ATMOSPHERIC PRESSURE

Silicon materials	Catalyst (%)	I.T. (°C)	R.T. (°C)
Si (A)		205	103, 172, 223, 298
Si (A)	Cu(3)	180	105, 146
Si (A)	Cu(10)	230	186
Si (A)	Cu(20)	236	119, 197
Si (B)		190	105
Si (B)	Cu(3)	178	106, 140, 218
Si (C)	Cu(3)	265	52, 172
Si—Al(8:2)		205	56
Si—Al(8:2)	Cu(5)	180	50
Si—Ca(3:7)		145, 180	100, 176
Si—Ca(3:7)	Cu(3)	165, (65)*	122, (85)*

* It appears as shoulder.

phenomena often had time lags and the precise points could not be determined by them. Therefore, only the temperature curve was chosen for determining the precise value. It was found from many observations that the I. T. value is not always the same in a contact mass, sometimes as much as 10°C difference, although it is always higher than R. T. The I. T. values obtained in the present experiment seemed to originate mainly from the composition of the materials or alloys of the contact masses tested, even though these values fluctuated somewhat with the changes of the particle surfaces. As to the R. T. value, there are more than two values for some samples of silicon metal or alloy. Moreover, as was seen in many observations, the 50, 105, 145 and 170°C points are prominent and sometimes common to the same kind of contact mass species. They seemed to correspond to the R. T. as shown in the following reaction Eqs. A, B, C and D.

$$\text{Al (in solid phase Si—Al)} + \text{HCl} \xrightarrow{50^\circ\text{C}} \text{AlCl}_3 + \text{H}_2 \quad \text{(A)}$$

$$\text{Fe (in solid phase Si—Fe)} + \text{HCl} \xrightarrow{105^\circ\text{C}} \text{FeCl}_2 + \text{H}_2 \quad \text{(B)}$$

$$\equiv\text{Si—Al} = \text{(in solid phase Si—Al)} + \text{HCl} \xrightarrow{145^\circ\text{C}} \equiv\text{Si—H} + = \text{AlCl} \quad \text{(C)}$$

$$\equiv\text{Si—}\underset{|}{\underset{|}{\text{Si}}}\text{—H} + \text{HCl} \xrightarrow[\text{AlCl}_3 \text{ present as catalyst}]{170^\circ\text{C}} \equiv\text{Si—H} + \text{ClSiH} \quad \text{(D)}$$

The following is a brief explanation to substantiate this relation. As is seen in

Table IX, Si (C)[11] and Si—Al alloy have almost the same R. T. at 50°C, as in the case of the metallic aluminum and hydrogen chloride reaction[12]. Therefore, Eq. A, which mainly concerns the presence of metallic aluminum in the contact mass, was given for the 50°C value. By the same speculation, 105°C value corresponding to the iron component which exists as the other main impurity in most silicon metal or silicon alloys, is indicated by Eq. B[13], the 145°C value has been assigned to Eq. C[5] by the authors. In almost all the reactions the forming of chlorosilane actually began at 170°C. Thus it was plausible that Eq. D was adequate for this R. T. value.

It was very interesting and important that when a small amount of anhydrous aluminum chloride was added to the contact masses as mixture or as vapor, the I. T.'s of these reactions were depressed close to the R.T.'s of their own. The fact that the commercial silicon Si(A)—fairly rich in aluminum ingredient—had a good yield of liquid product (Table I), might be proved by the above effect of aluminum chloride. Because in this reaction system the aluminum chloride could be easily derived from the reactions shown as Eqs. A and C. However, the remarkable effect of copper to each contact mass could not be understood from the results of I. T. and R. T. Unexpectedly the copper was reasonably considered only to promote the rate of this reaction.

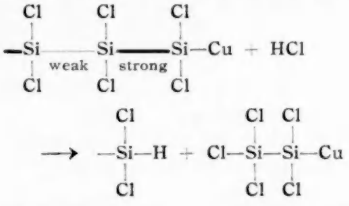
Discussion

The results of this experiment mentioned above and an assumption which will be proposed afterward afford the following reaction mechanism of the formation of chloropolysilane, i.e., the activation and main course stages for the reaction between commercial silicon and hydrogen chloride which gave monosilanes were explained as the formulae A, B, C and D mentioned above, but by those mechanisms alone no important part of the mechanism of forming chloropolysilane using copper catalyst could be explained. It might be reasonable to assume that copper combines with Si—H bond on the silicon mass which is formed as an intermediate of the C or D reactions (see Table VI):

$$\equiv SiH + Cu \xrightarrow[AlCl_3\ \text{catalyst}]{150^\circ C} \equiv Si—Cu + 1/2\ H_2 \qquad (E)$$

Hence, the co-catalytic action of aluminum chloride, produced by A and C reactions in the above reaction, is seen in the comparison of the experiments No. 1 and 2 in Table VI. Therefore, apart from the before mentioned I. T. depressing effect of aluminum chloride, it is preferable to use commercial silicon metal which has a small amount of aluminum as impurity or the vapor of aluminum chloride purposely conducted to the reaction zone of the pure silicon metal.

The authors have proposed the following assumption for the catalytic action of copper, i.e., the silicon-silicon bond which is adjacent to the silicon-copper bond formed by E reaction is difficult to be cleaved by hydrogen chloride as was shown in the above-mentioned results and the supposed cleavage is as follows:



This assumption may also facilitate the understanding of the mechanism of the chlorodisilane formation, and the catalytic action of copper for the present reaction. This unequalness of silicon-silicon bond strength may well be explained by the unequal electron density on the silicon atoms like the alternative strength-change theory of carbon bonds proposed by Ingold. If this assumption is correct at all, the reasons for the large yield of chlorodisilane in the main course of reaction by addition of a few per cent of copper and its sharply diminished formation at the final stage of the reaction may also be plausible. Hence, the copper content at the surface of the contact mass at the final stage may become so high that the copper atoms can be distributed enough through the adjacent silicon atoms.

11) As was mentioned Si (C) was originated from the Si-Al alloy. It was somewhat curious that Si (A), Si (B) which had more aluminum content than Si (C) did not show this 50°C R. T. value. However, this may be explained by the fact that iron masked the free aluminum character, perhaps by forming some kind of alloy.

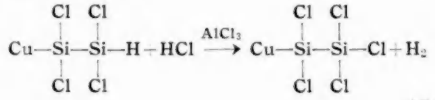
12) J. Iyoda and I. Shiihara, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), in press.

13) Generally speaking, the iron component in a silicon alloy must form some intermetallic compounds with silicon, but here in these contact masses, part of it combined with aluminum, forming some kind of easily reactive alloy.

The reaction between a typical silicon-copper bond and hydrogen chloride is shown as follows:

$$\equiv Si{-}Cu + HCl \longrightarrow \equiv Si{-}H + CuCl \qquad (F)$$

This reaction can also explain the formation of much H_3SiCl when a large amount of copper is added as catalyst. However, the reason for the meager existence of Si—H bond in chloropolysilane product seems to be plausible when the hydrogen chloride exchange reaction with some species of compounds on contact mass is assumed. A typical reaction can be considered:



(G)

The reverse reaction of F about the Si—H in the above compound is excluded from the results of experiments No. 3 and 4 in Table VI, and the possibility of E reaction of the Si—H is also taken to be small, since the chance of Si—H in this compound fixed on contact mass coming in contact with copper metal is supposed to be slight.

Also, the reaction of silicon and cuprous chloride is excluded under the reaction temperature of this experiment as 215°C, which is far from the R.T. value[14] (295°C) of this reaction.

$$\equiv Si{-}Si{\equiv} + CuCl \xrightarrow{\text{R.T. } 295^\circ C} \equiv Si{-}Cu + {\equiv}Si{-}Cl \qquad (H)$$

Therefore, cuprous chloride produced by F reaction may be reduced[15] mainly by hydrogen formed by E and G reactions.

$$2CuCl + H_2 \longrightarrow 2Cu + 2HCl \qquad (I)$$

And so regenerated metallic copper can be recycled to E reaction.

Summary

The copper catalyzed reaction of silicon metal powder with hydrogen chloride by flow method was studied in order to find a convenient preparative method of chloropolysilane, and also to elucidate the mechanism of this reaction.

This reaction was found to start at about 170~230°C, and once the reaction occurred, the contact mass is activated and the reaction takes place even at 170°C. When the most adequate conditions were adopted, chloropolysilanes were obtained in the condensate as efficiently as 30 wt.% yield based on hydrogen chloride.

As to the mechanism of the reaction, it seems to be plausible that the first step of the reaction is an attack of hydrogen chloride on aluminum which is usually present in the commercial silicon metal. The second step is the reaction between silicon hydride, which is derived from the first step reaction upon the silicon contact mass and metallic copper forming the silicon-copper bonding. The third step is the cleavage reaction of copper-activated silicon by hydrogen chloride to produce chlorosilanes under the presence of aluminum chloride. The aluminum chloride is also derived from the first step reaction, and copper is regenerated in metal form which can circulate among the latter two reaction steps as long as the effective silicon component is present.

The authors are indebted to Mr. S. Hara of their Institute for the analyses of residual masses, and to Mr. H. Takahashi of their laboratory for the analysis of siliconhydride.

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14) Details will be published before long. About the formation of Si-Cu bond presented before the 7th Annual Meeting of Chem. Soc. of Japan, April 3, 1954, Paper No. 7075 by Shiihara.

15) M. Rubalkin, *J. Russ. Phys. Chem.*, **21**, 155 (1889).

The Study of the Adsorption of Detergents at a Solution-Air Interface by Radiotracer Method. III. The Effect of Inorganic Electrolytes on the Adsorption of Sodium Dodecyl Sulfate

By Ryohei MATUURA, Hideo KIMIZUKA and Katsumasa YATSUNAMI

(Received November 17, 1958)

Roe and Brass[1], Nilsson[2] and Salley et al.[3] have checked the Gibbs adsorption equation with potassium palmitate, sodium dodecyl sulfate and Aerosol OTN in the presence of potassium hydroxide, sodium chloride and Aerosol OT, respectively. They have obtained the result that the adsorption of detergent at the air-solution interface takes place in accordance with the Gibbs adsorption equation. It was suggested also through the observation of the change with time in surface tension of detergent solution that the addition of excess electrolytes increases the adsorption rate of surface active ion[4].

However, the adsorption isotherm and adsorption rate for the detergent solution in the presence of various electrolytes, especially in the presence of the salts containing no common ion with the detergent, has not yet been measured directly. In the present study, we have succeeded by the aid of the radiotracer method in measuring directly the adsorption of dodecyl sulfate ion (abbreviated as DS^-) at the solution-air interface from the solutions containing sodium dodecyl sulfate (abbreviated as SDS) and excess inorganic electrolytes. The surface tension of the solution has been measured and the Gibbs adsorption equation has been checked.

Experimental

Materials. — The radioactive SDS used was synthesized as described in the preceding paper[5]. Of the inorganic electrolytes, manganous and aluminum chlorides were those of extra pure reagents and purified by recrystallization, while sodium, potassium and magnesium chlorides were those of guaranteed reagents and used without further purification. For the preparation of the solution under investigation, SDS was dissolved in the aqueous solution of respective inorganic electrolyte with a given concentration.

Method.—The procedure used for the measurement of the surface excess of DS^- was the same as described in the preceding paper[5,6]. The surface count of radioactive sodium sulfate solution was taken as the same as that of the bulk of radioactive SDS solution, both containing excess of salts.

The surface tension measurement was carried out by means of the du Noüy tensiometer. The temperature of the experiment was maintained at 29±1°C.

Results and Discussion

It was found that the adsorption of DS^- in the presence of excess salts with or without common ions was so rapid that

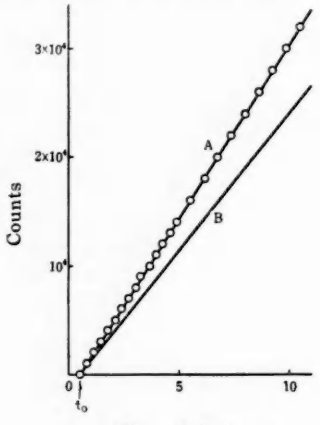

Fig. 1. Count vs. time relation for the solution A containing 5.543×10^{-4} mol./l. SDS and 0.3 N NaCl and the solution B containing 5.543×10^{-4} mol./l. Na_2SO_4 and 0.3 N NaCl, 29±1°C.

1) C. P. Roe and P. D. Brass, *J. Am. Chem. Soc.*, **76**, 4703 (1954).
2) G. Nilsson, *J. Phys. Chem.*, **61**, 1135 (1957).
3) H. Sobotka, "Monomolecular Layers", The American Association for Advancement of Science, Washington, D. C. (1954), p. 81.
4) N. K. Adam and H. L. Shute, *Trans. Faraday Soc.*, **34**, 758 (1938); K. S. G. Doss, *Kolloid-Z.*, **86**, 205 (1939); G. C. Nutting, F. A. Long and W. D. Harkins, *J. Am. Chem. Soc.*, **62**, 1946 (1940).
5) R. Matuura, H. Kimizuka, S. Miyamoto and R. Shimozawa, This Bulletin, **31**, 532 (1958).
6) R. Matuura, H. Kimizuka, S. Miyamoto, R. Shimozawa and K. Yatsunami, ibid., **32**, 404 (1959).

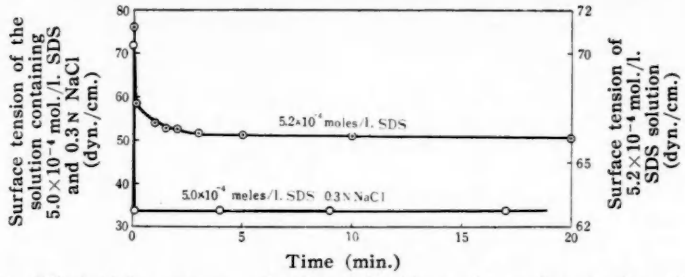
Surface tension of the solution containing 5.0×10^{-4} mol./l. SDS and 0.3 N NaCl (dyn./cm.)
Surface tension of 5.2×10^{-4} mol./l. SDS solution (dyn./cm.)
5.2×10^{-4} moles/l. SDS
5.0×10^{-4} meles/l. SDS 0.3 N NaCl
Time (min.)

Fig. 2. Effect of the presence of sodium chloride on the surface tension of SDS solution, 29±1°C.

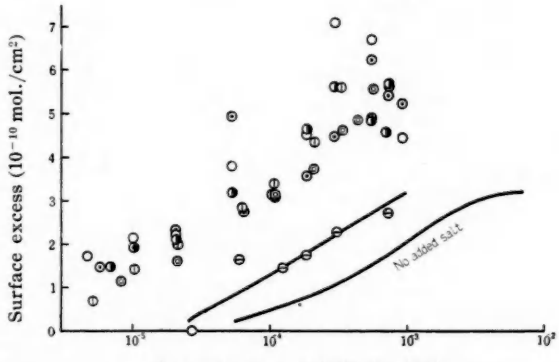

Fig. 3. Effect of addition of sodium chloride on the adsorption of DS^-, 29±1°C.
⊖ 0.01 N NaCl, ◎ 0.1 N NaCl, ◑ 0.2 N NaCl, ◑ 0.3 N NaCl, ⊙ 0.5 N NaCl, ○ 1.0 N NaCl.

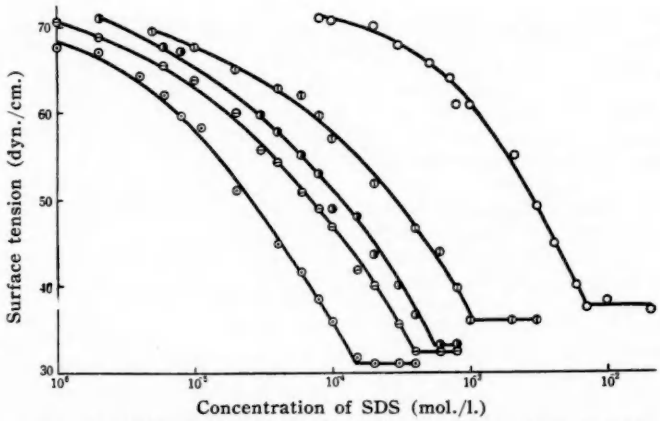

Fig. 4. Effect of added sodium chloride on the surface tension of SDS solution, 29±1°C. Numericals in this figure show the concentration of sodium chloride in N.
○ no added NaCl, ◑ 0.1 N NaCl, ◑ 0.3 N NaCl, ⊖ 0.5 N NaCl, ⊙ 1.0 N NaCl.

the equilibrium was attained within one minute, while without added salts it took several minutes or more to reach the adsorption equilibrium at the solution-air interface as was reported in the preceding paper[5]. Fig. 1 is an example of counts vs. time relation of SDS solution (concentration is 5.543×10^{-4} mol./l.) containing 0.3 N sodium chloride. t_0 in Fig. 1 is the starting time of counting. It is seen that a linear relation is held between count and time, showing that the adsorption has already reached equilibrium at the starting time (t_0) of counting. It has already been known that the presence of inorganic salts makes faster the attainment of equilibrium of surface tension of the detergent solution[4]. In the present study, the effect of the presence of sodium chloride on the change with time of surface tension of SDS solution was also measured by means of the Wilhelmy plate method. Fig. 2 shows an example of the effect of the presence of sodium chloride on the rate of surface tension lowering. It may easily be seen that the presence of salt not only makes faster the attainment of equilibrium of surface tenstion, but also lowers the surface tension value. Furthermore, it may be pointed out that in the presence of salt the surface tension almost reaches equilibrium even at the starting time of experiment. The present experiment, therefore, clearly shows that the rapid rate of surface tension lowering actually corresponds, as might be expected, to the rapid rate of adsorption at least qualitatively. However the rate of adsorption was too rapid to measure precisely and so the quantitative relation between the surface tension lowering and the adsorption before reaching equilibrium could not be determined in the present study. The results and discussions below therefore are concerned only with the equilibrium state of adsorption and surface tension.

First the effect of sodium chloride of various concentrations on the adsorption of DS^- was measured and the result is shown in Fig. 3. It is obvious that the presence of excess sodium chloride increases the adsorption of DS^- considerably. Here it is to be noted that, although below 0.1 N of sodium chloride the adsorption of DS^- increases with the concentration of the salt, above 0.1 N of sodium chloride the values of surface excess of DS^- fall within a range almost independent of the concentration of the salt. On the contrary, the surface tension of SDS solution containing sodium chloride decreases regularly with the concentration of the salt up to 1 N, as shown in Fig. 4.

When the Gibbs adsorption equation for the solution of surface active electrolyte is written in the form

$$\Gamma = -\frac{1}{nRT}\frac{\partial\gamma}{\partial \ln C}$$

where Γ is the surface excess, γ, surface tension, C, concentration of the detergent and R and T are gas constant and temperature, respectively. n is expected, from theoretical considerations, to be unity in the presence of large excess of salts

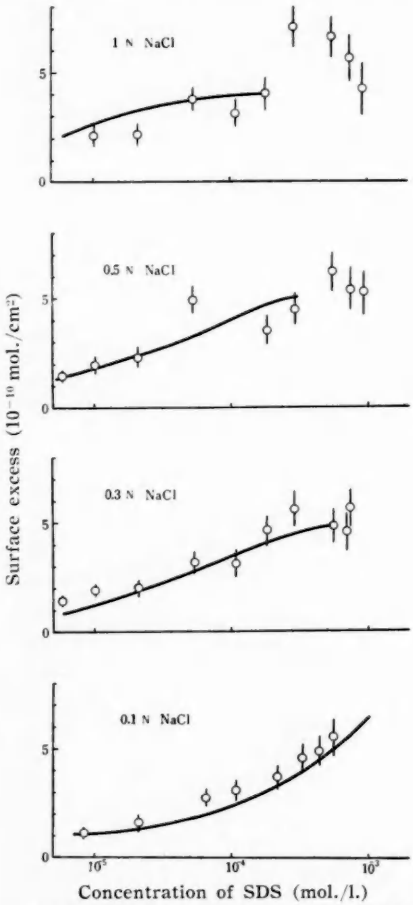

Fig. 5. Adsorption of DS^- from SDS solution containing sodium chloride. Full lines represent calculated relations from surface tension vs. logarithmic concentration curves by using the Gibbs adsorption equation of $n=1$.

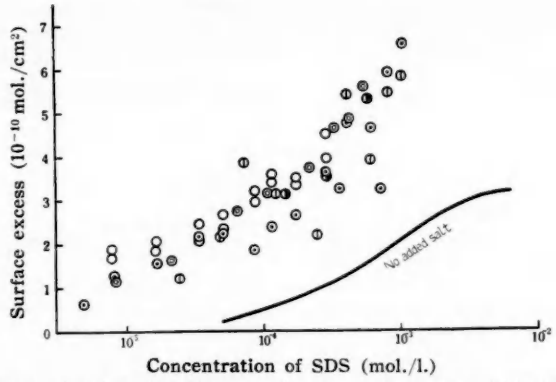

Fig. 6. Effect of added electrolytes on the adsorption of DS^-, $29\pm1°C$. Concentration of electrolytes are all 0.1 N.
◎ NaCl, ◑ KCl, ⊙ $MgCl_2$, ⓘ $MnCl_2$, ○ $AlCl_3$.

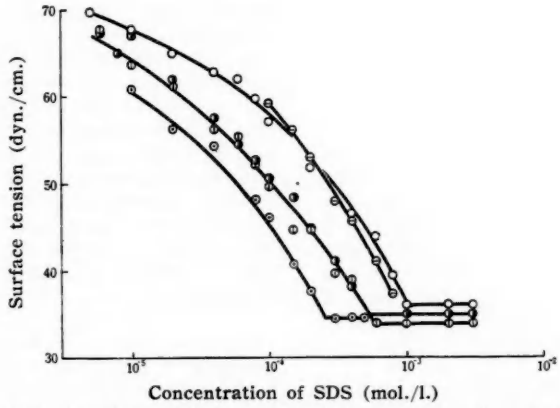

Fig. 7. Effect of added electrolytes on the surface tension of SDS solution, $29\pm1°C$. Concentrations of electrolytes are all 0.1 N.
○ NaCl, ⊖ KCl, ◑ $MgCl_2$, ⓘ $MnCl_2$, ⊙ $AlCl_3$.

or alkalis[5]. From the data in Fig. 4 we can calculate Γ of DS^- in the presence of sodium chloride and check the Gibbs equation*. The results are shown in Fig. 5 for various concentrations of sodium chloride. From these figures it is reasonable to conclude that the Gibbs adsorption equation of $n=1$ is a fair expression for the adsorption of DS^- below cmc in the presence of sodium chloride.

Next the effect of various inorganic electrolytes having no common ion with the detergent was measured. Some salts made precipitates even in the dilute solution of the detergent and so the kinds of salts investigated were limited. The salts used in the present experiment were potassium chloride, magnesium chloride, manganous chloride and aluminum chloride and SDS was dissolved in the aqueous solution of each electrolyte of the concentration of 0.1 N. The relation between the surface excess of DS^- and SDS concentration in the presence of 0.1 N inorganic electrolytes is shown in Fig. 6. From this figure we can see that the presence of excess of inorganic salts makes considerable increase in the adsorption of the detergent, regardless of the type of the salts added.

* Strictly speaking, the concentration in the Gibbs equation should be replaced by the activity. However it may not cause serious errors to use concentration instead of activity *below cmc* of the detergent even in the presence of excess salt as in the present experiment[2,3].

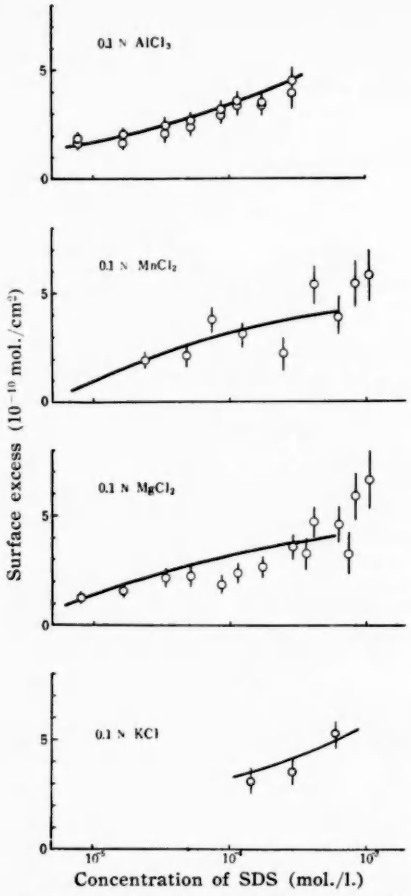

Fig. 8. Adsorption of DS^- from SDS solution containing 0.1 N excess of salt. Full lines represent calculated relations from surface tension vs. logarithmic concentration curves by using the Gibbs adsorption equation of $n=1$.

The surface tension vs. concentration relation of these systems is shown in Fig. 7. It is interesting to note that the surface tension decreases regularly with the valency of cation of added salts, while the surface excess shows no such regular relations.

Using the data in Fig. 7, the surface excess was calculated by the Gibbs equation putting $n=1$ and compared with the observed value. The results are plotted in Fig. 8. From these results it will be possible to say that the Gibbs equation of $n=1$ represents approximately the experimental values of surface adsorption of DS^- even in the presence of inorganic salts having no common ions with the detergent.

Summary

The direct measurement of the adsorption of ^{35}S labelled dodecyl sulfate ion at the solution surface and the measurement of the surface tension were carried out on the aqueous solutions of sodium dodecyl sulfate containing a given concentration of an excess salt. The salt concentrations studied were 0.01, 0.1, 0.3, 0.5 and 1 N for sodium chloride, and 0.1 N for potassium-magnesium, manganous and aluminum chlorides.

1. The adsorption of dodecyl sulfate ion reaches equilibrium within one minute for all the systems under investigation.
2. The presence of excess of salt gives rise to the remarkable increase in the adsorption of dodecyl sulfate ion, but at the concentrations of excessive salts of about 0.1 N or more, the effects of the concentration and nature of the salts on the adsorption of dodecyl sulfate ion are not so appreciable.
3. The adsorption of dodecyl sulfate ion was well expressed by the Gibbs adsorption equation of $n=1$ for the systems under investigation.

In conclusion the authors express their hearty thanks to Professor T. Sasaki of Tokyo Metropolitan University for his kind advice and encouragement in the course of this study. The cost of this study was defrayed from the Chemical Research Grant of the Ministry of Education, to which the authors' thanks are also due.

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SHORT COMMUNICATIONS

Polymerization of Methyl Methacrylate Initiated by a Combined Action of Di-p-tolyl Disulfoxide, Dimethylaniline and Oxygen in Air

By Ryoichi UEHARA

(Received February 27, 1959)

The effects of *p*-toluenesulfinic acid (TSA) upon polymerization of vinyl monomers have been noted by Hagger[1] and Bredereck[2]. In a previous paper by the present author[3], results of studies on the kinetics of the polymerization of methyl methacrylate (MMA) initiated by the system of TSA, dimethylaniline (DMA) and oxygen in air have been reported. The polymerization was initiated at room temperature by means of this system. TSA is not so stable even at room temperature, and by being left in air changes into *p*-toluenesulfonic acid (TSOA), di-*p*-tolyl disulfoxide (DTDS) and water through the following reaction[4]:

$$3CH_3C_6H_4SO_2H = CH_3C_6H_4SO_3H + (CH_3C_6H_4SO)_2 + H_2O$$

Owing to this deterioration, the activity of TSA as a component of the initiating system of the room-temperature polymerization of MMA is reduced gradually[5]. The present author has examined the effects of TSOA and DTDS upon the polymerization of MMA at various temperatures, and found that the polymerization was initiated by a combined action of DTDS, DMA and oxygen in air at above 60°C. TSOA could not initiate the polymerization in combination with DMA and oxygen. It has been found by the present author that several compounds related to TSA, e.g., *p*-tolyl methyl sulfone[6] and di-*p*-tolylsulfonylhydroxylamine[6], initiated the polymerization of MMA in combination with DMA and oxygen. DTDS is a new material which belongs to this group of compounds. In the present communication, some results of experiments are given. The nature of the effects of the polymerization-initiating system will be discussed in future.

In Table I, per cent conversions after 1 hr. at various temperatures are given (DTDS 2.34×10^{-2} mol./l. and DMA 2.58×10^{-2} mol./l. in air). For the initiation of the polymerization, the coexistence of the three components of the initiating system was necessary. Namely, in the cases when MMA was heated at 70°C with DTDS 2.51×10^{-2} mol./l. and DMA 2.52×10^{-2} mol./l. in the atmosphere of nitrogen or with DTDS 2.48×10^{-2} mol./l. alone in air, no polymerization took place, and when DMA 2.52×10^{-2} mol./l. alone was employed in air, only trace of polymethyl methacrylate (PMMA) was obtained after 3 hr. at 70°C. In Fig. 1, per cent conversions of the bulk polymerization of MMA at 70°C in air (DTDS 2.16×10^{-2} mol./l. and DMA 2.20×10^{-2} mol./l.) are plotted against the time of polymerization. A time conversion curve of the polymerization by means of benzoyl peroxide (BPO, 2.0×10^{-2} mol./l.) in nitrogen is shown by the dotted line in the figure. From the beginning of

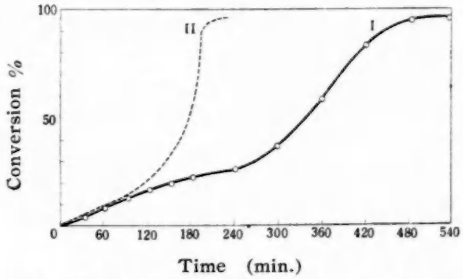

Fig. 1. Time versus conversion curve of bulk polymerization of MMA at 70°C in air. I, DTDS 2.16×10^{-2} mol./l. and DMA 2.20×10^{-2} mol./l. II, BPO 2.0×10^{-2} mol./l. (under nitrogen).

1) O. Hagger, *Helv. Chim. Acta*, **31**, 1629 (1948).
2) H. Bredereck et al., *Ber.*, **89**, 731 (1956).
3) R. Uehara, Submitted to this Bulletin for publication., **32**, No. 9 or 10 (1959).
4) C. Pauly and R. Otto, *Ber.*, **10**, 2128 (1877).
5) C. E. Schildknecht, "Polymer Processes", Interscience, New York, (1956), p. 61.
6) R. Uehara, Submitted to this Bulletin for publication, **32**, No. 9 or 10 (1959).

the polymerization until the conversion reached to 15%, the rate of polymerization initiated by the system of DTDS, DMA and oxygen was only slightly smaller than that of the polymerization by BPO. After this period, the polymerization initiated by the system of DTDS, DMA and oxygen proceeded at a moderate rate and somewhat acceleratively in the final period, while the polymerization by BPO run quite acceleratively and almost explosively at the final stage. In the polymerization initiated by the system of DTDS, DMA and oxygen, the conversion reached to 90% after 450 min. from the beginning of the reaction, but in case of the polymerization by BPO the conversion reached to the same extent after 190 min. In the bulk polymerization of MMA, gelation of the reacting system occurs when the conversion reaches to 20~30%. So, it is very probable that the polymerization initiated by the system of DTDS, DMA and oxygen does not proceed so acceleratively owing to the fact that the rate of diffusion of oxygen from air into the reacting system is reduced due to the gelation. On the other hand, DTDS alone did not affect upon the polymerization of MMA initiated by BPO under nitrogen, i. e., per cent conversion after 1 hr. and the degree of polymerization (DP) of PMMA were not changed by the addition of DTDS (Table I).

TABLE I. RESULTS OF THE BULK POLYMERIZATION OF METHYL METHACRYLATE

Atmosphere	Initiator (mol./l.×10²)	°C	% Conversion after 1 hr.	DP
Air	[DTDS(2.34) DMA(2.58)]	40	0	
Air	[DTDS(2.34) DMA(2.58)]	50	1.5	
Air	[DTDS(2.34) DMA(2.58)]	60	3.7	4900
Air	[DTDS(2.34) DMA(2.58)]	70	8.7	2850
Air	[DTDS(2.34) DMA(2.58)]	80	17.4	1390
Air	DTDS(2.48)	70	0*	
Air	DMA(2.52)	70	trace*	
Nitrogen	[DTDS(2.51) DMA(2.52)]	70	0*	
Nitrogen	BPO(2.0)	70	10.3	3900
Nitrogen	[BPO(2.0) DTDS(2.51)]	70	10.9	3780

* After 3 hr.

Experimental — DTDS was prepared by heating TSA (20 g.) with water (60 cc.) in a boiling water bath. TSA was dissolved and then an oily material separated gradually. After 5 hr., the oil was washed with 5% aqueous sodium hydroxide and pure water, and cooled. Crude DTDS was recrystallized three times from a mixture of methanol and ether (1 : 1 by volume), and pure DTDS (6.5g.) was obtained, m.p. 78.5°C. Purification of MMA and DMA have been mentioned in a previous paper[7]. The polymerization in air and under nitrogen were carried out respectively in open test tubes[8] and sealed tubes[7]. DTDS and DMA were dissolved in MMA cooled in an ice-salt bath. The solution (5 cc.) was placed in a test tube and heated with shaking. Per cent conversion of the polymerization was estimated from the weight of PMMA. Details of the procedures have been given previously[7]. DP of PMMA was calculated from the intrinsic viscosity in chloroform by using the equation of Sakurada[8].

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7) R. Uehara, This Bulletin, **31**, 685 (1958).
8) I. Sakurada, *Chem. High Polymers (Kobunshi Kagaku)*, **2**, 253 (1945).

On the Concentration Potential

By C. V. SURYANARAYANA and V. K. VENKATESAN*

(Received April 2, 1959)

Vaidhyanathan[1] is in great error in his 'Remarks on the composition potential' in regard to a quantity defined by us[2] recently. We defined a quantity C_p as the ratio of the mole fraction of the solute at any given molal concentration to that at saturation at the same temperature. Precisely we called this ratio C_p, the concentration potential and not the composition potential as he states in his remarks. What is most amusing is that Vaidhyanathan imagines that we have stated the above ratio as being a truly thermodynamic potential. We have not done so. A careful perusal of our paper (loc. cit.) shows that the wording is as follows:

"The concentration potential newly conceived herein is a truly thermodynamic *concept of concentration* dependent only on

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1) V. S. Vaidhyanathan, This Bulletin, **32**, 99 (1959).
2) C. V. Suryanarayana and V. K. Venkatesan, ibid. **31**, 442 (1958).

the initial and final states of stability of a solution and independent of any arbitrary scale of concentration or the nature of both the solvent and the solute". The *concept* is a thermodynamic one as explained by the rest of the above sentence but definitely it can never even imply that the ratio called by us 'concentration potential' is ever a thermodynamic potential at all.

We must point out incidentally that the definition of thermodynamic potentials given naively by Vaidhyanathan is in serious error. He states: "The potentials that can be defined as 'thermodynamic potentials' and which conform to this statement are the Gibbs and Helmholtz functions, energy, enthalpy, entropy and the chemical potential and they alone". Excepting the last mentioned chemical potential which is the derivative of the Gibbs free energy with respect to the number of moles of the species at constant temperature and pressure all the other functions are extensive properties and are not called thermodynamic potentials merely by themselves. They have of course the properties of exact differentials. Thermodynamic potentials are always intensive[3] (expressed per mol.) especially for the chemist when dealing with solutions. Further what he states in the first part of his last para has either no purpose or contradicts the last part of his first para and hangs loosely.

What may be really a pertinent question is the reason why we have called the newly defined ratio a concentration potential. An answer to this is due to appear elsewhere (under publication), and is briefly as follows. When we picture what happens when a soluble solid solute is added to a solvent, we can imagine its dissolution at any instant giving in the vicinity of the solute a successive series of layers of solutions, the most concentrated one being nearest the solid and the least concentrated one the pure solvent itself. The most concentrated one is the saturation concentration and the lowest concentration is zero. In between, there is to be imagined a concentration gradient. It is so clear that the saturation concentration has a directive influence on the concentration gradient. Our main purpose in defining this new ratio is to indicate the soundness of comparing a physical property of solutions of two different solutes in a given solvent at identical gradients and not at identical arbitrary concentrations as is being done so far. In this context any arbitrary concentration between the saturation and zero values has been visualized as better represented by the ratio of mole fraction to that at saturation and called the concentration potential due to its relation to the above mentioned gradient. Any arbitrary concentration for a salt must occur in the concentration gradient given in the above picture of the dissolution of the same salt. The situation is similar to the well-known classical law of corresponding states. But it is too early to predict the usefulness of the newly defined ratio, especially whether equally important generalizations will accrue out of the use of C_p. Of course, C_p has the properties of an exact differential between the limits of zero concentration and saturation.

Again Vaidhyanathan states that apart from the fact that C_p is an intensive variable and is dimensionless, no other thermodynamic significance can be attributed to it. We should say that the above reasons are not enough to say that no other thermodynamic significance can be attributed to it. An understanding of the thermodynamic significance of the saturation state of a solution will be the final deciding factor in assessing the thermodynamic significance of the concentration potential defined by us. A perusal through Walden[4], van Laar[5], and Ricci and Davis[6] indicates enough thermodynamic importance of the saturated state.

In this back ground, though we should have no objection to call the concentration potential by any other name for any good reasons, we fail to see why it should not be called so as at present.

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3) E. A. Guggenheim, "Thermodynamics", North Holland Publ. Co., Amsterdam, (1957).

4) P. Walden, *Z. physik. Chem.*, **54**, 129, **55**, 683 (1906).
5) J. J. van Laar, ibid., **58**, 567; **59**, 212 (1907).
6) J. E. Ricci and J. W. Davis, *J. Am. Chem. Soc.*, **62**, 407 (1940).

A Transannular Beckmann Rearrangement in Liquid Sulfur Dioxide

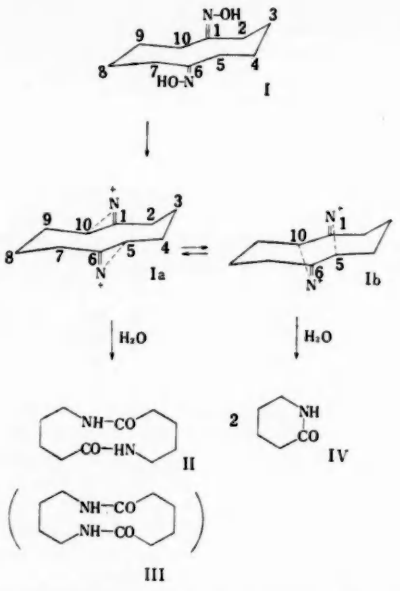
By Niichiro Tokura, Ritsuro Tada and Kunio Suzuki

(Received April 15, 1959)

In medium sized alicyclic compounds, transannular reactions have often been observed[1-3]. This communication is concerned with an abnormal Beckmann rearrangement, the nature of which should be attributed to a novel transannular type of reaction.

When cyclodecane-1, 6-dione dioxime (I) reacted with sulfur trioxide in liquid sulfur dioxide at room temperature for twelve hours, followed by elimination of sulfur dioxide by evaporation and addition of ice water to the reaction residue, a hitherto unreported cyclic oligomer of δ-valerolactam, 1, 7-diaza-6, 12-dioxocyclododecane (II) (yield 75%), separated out as fine crystals, m.p.(purified by sublimation) 264~266°C (Found: N, 13.9%. Calcd. for $C_{10}H_{18}O_2N_2$: N, 14.1%; mol. wt. Found: 215. Calcd. 198; ninhydrin test, negative[4]; I. R. ν_{max}^{KBr}: 1650 (CO), 3280 (NH) cm^{-1}). The I. R. spectrum of II closely resembles the spectra of cyclic oligomers of ε-caprolactam[4]. As we could find no diamine or dicarboxylic acid in the acid hydrolyzed product of II, absence of III (another possible product of rearrangement) in the reaction mixture was proved.

However, when the reaction was carried out with thionyl chloride in place of sulfur trioxide in liquid sulfur dioxide similarly as described above, followed by extraction with chloroform and evaporation of the solvent, I afforded a brown viscous nitrogen-containing liquid (27%), the structure of which was difficult to be identified. The residual solution after the extraction was made slightly alkaline with sodium hydroxide and again extracted with chloroform. The chloroform solution was condensed and the residue was subjected to distillation in vacuo. A yellow oil(IV) b.p. 90~93°C(2mmHg) was obtained. IV was identified as δ-valerolactam (33%),



n_D^{17}=1.5339 (Found: N, 13.8%. Calcd. for C_5H_9ON: N, 14.1%, N-(4-carboxyl butyl) phthalimide, m. p. and mixed m. p. with an authentic specimen, 117.5~118.5°C[5]). Its I. R. spectrum also coincided with that of IV described in the literature[6]. That δ-valerolactam (IV) was not a secondary product derived from II was demonstrated when II reacted in liquid sulfur dioxide with thionyl chloride at room temperature. No appreciable formation of IV was observed.

As the distances between the nitrogen atoms and carbon atoms (C_5 and C_{10}) are sufficiently close to permit an equilibrium state between the structures Ia and Ib, the latter being favored by thionyl chloride, the completion of the rearrangement, involving cleavage of C_1-C_{10} and C_5-C_6 linkages, gives rise to formation of IV. In such a case, a transannular Beckmann rearrangement is the most plausible explanation for the formation of IV from I in liquid sulfur dioxide.

The authors wish to thank the Befu Chemical Industries Co. for the donation of liquid sulfur dioxide.

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1) P. A. Plattner and J. Hulstkamp *Helv. Chim. Acta*, **27**, 220 (1944).
2) A. C. Cope, S. W. Fenton and C. F. Spencer, *J. Am. Chem. Soc.*, **74**, 5885 (1952).
3) V. Prelog, K. Schenker and W. Kunig, *Helv. Chim. Acta*, **36**, 471 (1953).
4) H. Zahn et al., *Angew. Chem.*, **68**, 231 (1956).
5) M. Taniyama et al., *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **59**, 545 (1956).
6) W. Schneider, *Ann*, **590**, 155 (1954).

NMR Spectra of Formals, Acetals and the Related Compounds

By Kenkichi NUKADA and Utako MAEDA

(Received April 22, 1959)

It is interesting to study the NMR spectra of formals (R_1-O-CH_2-O-R_2), acetals (R_1-O-CH(CH_3)-R_2) and the related compounds (H-C(OR)$_3$ and R-(O-CH_2-CH_2)$_n$-OR), as these compounds contain functional groups such as CH_3-O, CH_3-CH_2-O, O-CH_2-CH_2-O, O-CH_2-O, H-C-CH_3, etc. It is quite

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difficult, or sometimes perfectly impossible, to identify some of these functional groups by the infrared spectroscopy[1]. We have tried to identify them by the high resolution NMR spectroscopy[2]. JNM-3 (Japan Electron Optics Laboratory Co.) and 4300-B (Varian Associates) spectrometers were used.

Fig. 1 shows the NMR spectra of benzene solutions of several compounds except dimethyl acetal (CH_3-O-CH(CH_3)-O-CH_3), acetal (C_2H_5-O-CH(CH_3)-O-C_2H_5) and diethylene-glycol diethyl ether (C_2H_5-(O-CH_2-CH_2)$_2$-O-C_2H_5). The spectra of these three compounds were obtained in pure liquid phase and reference bands are shown with arrows on the peaks of each spectrum. The unit of abscissa means the chemical shift from the signal of benzene protons. The tentative assignments are shown on the tops of each peak.

TABLE I. THE VALUES OF CHEMICAL SHIFTS OF FUNCTIONAL GROUPS

Type of group	Chemical shift from benzene protons ($\times 10^{-7}$)
H-C(=O)(-O-)-O-	21.3
H-C(-O-)(-O-)-CH_3	27.5
O-CH_2-O	27.8±1.0
O-CH_2-C	37.8±2.0
CH_3-O	40.3±0.8
CH_3-C(-O-)(-O-)-H	62±2
CH_3-CH_2-O	61±3

1) K. Nukada, *J. Chem. Soc. Japan. Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), in press.

2) Chamberlain reported the NMR spectra of several hundreds of compounds including some ethers and alcohols, but in his paper those of above-mentioned compounds have not been reported. (N. F. Chamberlain, *Anal. Chem.*, 31, 56 (1959)).

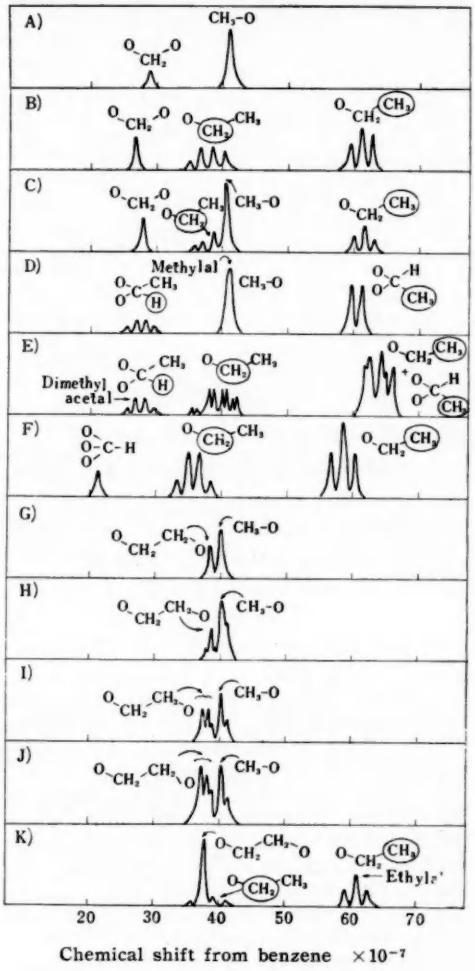

Fig. 1. Proton magnetic resonance spectra of formals, acetals and the related compounds.

A. Methylal. ($CH_3OCH_2OCH_3$)
B. Ethylal. ($CH_3CH_2OCH_2OCH_2CH_3$)
C. Methyl-ethyl formal. ($CH_3CH_2OCH_2OCH_3$)
D. Dimethyl acetal. ($CH_3OCH(CH_3)OCH_3$)
E. Acetal. ($CH_3CH_2OCH(CH_3)OCH_2CH_3$)
F. Orthoformic acid ethyl ester. ($CH(OCH_2CH_3)_3$)
G. Ethylene glycol dimethyl ether. ($CH_3OCH_2CH_2OCH_3$)
H. Diethylene glycol dimethyl ether. ($CH_3(OCH_2CH_2)_2OCH_3$)
I. Triethylene glycol dimethyl ether. ($CH_3(OCH_2CH_2)_3OCH_3$)
J. Tetraethylene glycol dimethyl ether. ($CH_3(OCH_2CH_2)_4OCH_3$)
K. Diethylene glycol diethyl ether. ($CH_3CH_2(OCH_2CH_2)_2OCH_2CH_3$)

We wish to express our sincere thanks to Dr. Y. Mashiko of this Institute, Dr. S. Hattori of Kanazawa University and Dr. T. Seki of Japan Electron Optics Laboratory Co. for their kind advice and to Dr. H. Honda and Dr. K. Nagata of the Resources Research Institute who kindly measured a part of spectra.

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A New Compound of Tin(IV) with 8-Quinolinol and its Use in Gravimetric Analysis

By Hiroshi Hamaguchi, Nagao Ikeda and Kazuya Osawa

(Received May 8, 1959)

Shiba[1] reported that tin(II) was precipitated with 8-quinolinol (oxine) from dilute ammoniacal solution. As to the oxinate of tin(IV), Gentry and Sherrington[2] found that tin(IV) was extractable by oxine chloroform solution. They estimated the formula of the extractable oxinate of tin to be $Sn(C_9H_6NO)_4$. No report has been published, however, on the formation of a stable precipitate of oxine compound of tin(IV).

According to the present authors' experiments, tin(IV) is precipitated quantitatively from 0.2 N hydrochloric acid solution by adding oxine solution, but at the other concentrations of hydrochloric acid, the precipitation is not complete, as is shown in Fig. 1.

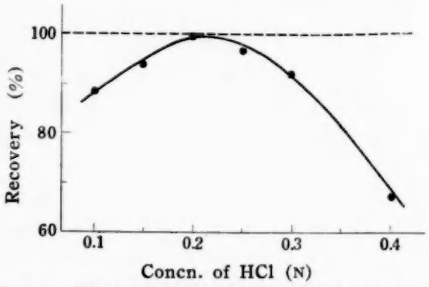

Fig. 1. Effect of hydrochloric acid concentration on the precipitation of tin(IV) oxinate.

The color of the precipitate is brilliant yellow. The compound is stable against heating at least up to 360°C. It is insoluble in mineral acid or alkaline solutions except for concentrated sulfuric acid. It is also insoluble in ordinary organic solvents. The chemical composition of the precipitate is as follows:

Anal. Found: Sn, 24.9; Cl, 15.2; C, 45.05; H, 2.63; N, 5.68*. Calcd. for $SnCl_2(C_9H_6NO)_2$; Sn, 24.8; Cl, 14.8; C, 45.2; H, 2.54; N, 5.87%.

The ionic species of tin(IV) in 0.2 N hydrochloric acid solution was examined by the aid of ion-exchange resin (Dowex 50), and it was found the charge of the species to be +2, which seems to justify the above mentioned chemical composition of the compound.

The application of this compound to the gravimetric determination of tin was then examined. The recommended procedure is the following.

Adjust the acidity to 0.2 N hydrochloric acid. Add the same volume of 2% oxine solution**. Keep the solution at 70~90°C for 1.5~2 hr. Filter with a glass filter, wash with 3 N hydrochloric acid, dry at 110~120°C and then weigh as $SnCl_2(C_9H_6NO)_2$.

Table I. Determination of tin as oxinate

Sn taken (mg.)	Sn oxinate (mg.)	Sn found (mg.)	Error (mg.)
1.00	3.5	0.87	0.13
1.99	8.0	1.99	0.00
2.99	11.9	2.96	0.03
4.98	19.2	4.77	0.21
9.96	39.5	9.81	0.15

Some results are shown in Table I. No metallic salt except molybdenum interferes. Bismuth and antimony should be absent because of their hydrolysis in the condition of the procedure. Presence of nitrate or phosphate leads to the hydrolysis of stannic ions. The precipitate of oxinate is not formed under the presence of tartrate.

1) Y. Shiba, *Repts. Gov. Ind. Research Inst. Tokyo*, **27**, No. 8, 12 (1932).
2) C. Gentry and L. Sherrington, *Analyst*, **75**, 17 (1950).

* The analyses of carbon, hydrogen and nitrogen were carried out at the Institute of Physical and Chemical Research.
** The oxine solution: Dissolve 6 g. of oxine in 5 ml. of concentrated hydrochloric acid, and dilute to 300 ml. with distilled water.

The authors wish to express their sincere thanks to Dr. Rokuro Kuroda for his helpful advice.

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*Chemical Shifts of the Proton Magnetic Resonance in Alkylhydroperoxides**

By Shizuo FUJIWARA, Mikio KATAYAMA and Shinichi KAMIO**

(Received May 12, 1959)

Chemical shifts of the proton magnetic resonance in alkylhydroperoxides were measured in order to obtain the NMR informations of these compounds which have not been reported. The samples are listed in Table I with their characteristic data. All of them except *tert*-butylhydroperoxide were synthesized by one of us (S. K.) according to the methods reported by Williams and Mosher[1]. The *tert*-butylhydroperoxide was obtained commercially from the International Chemical Company.

TABLE I. SAMPLES OF NMR MEASUREMENTS

n-Propyl hydroperoxide	35°C/20 mm.	$n_D^{25}=1.3890$
n-Butyl hydroperoxide	28~29°C/5 mm.	$n_D^{20}=1.4057$
sec-Butyl hydroperoxide	41~42°C/11 mm.	$n_D^{20}=1.4050$
n-Amyl hydroperoxide	41~42°C/4 mm.	$n_D^{20}=1.4146$
n-Octyl hydroperoxide	64~66°C/0.7 mm.	$n_D^{20}=1.4311$

tert-Butylhydroperoxide was obtained commercially.

The apparatus used for the measurements of the chemical shifts is the one constructed in this laboratory using the permanent magnet manufactured by the Indiana Steel Company and the resonant frequency is about 27.030 Mc. ($H_0=6300$ gauss). The chemical shift of the OOH proton resonance in each compound was measured as the separation from CH_3 signal appearing as the peak in the highest field on the recorded charts taking the cyclohexane and benzene mixture (0.28 g. +0.30 g.) as the reference to show the separation of 227 cps. at 40 Mc.

According to the results of the measurements, the resonant positions for the OOH protons are in the field lower than those for CH_3 by about 245 (±5) cps., being close to the value for COOH proton in aliphatic acid, 267 (±3) cps. for *n*-butylric acid, or about 280~230 cps.[2], and less shielded than the OH protons in alcohols which were measured as 120 (±5) cps. or 120~100 cps[2]. The propylhydroperoxide showed a very small value of 222 (±5) cps., and this was assumed to be due to the decomposition of the compound. The figures showing the variations of the observed data are due to the overlapping and the incomplete separation of the signals of CH_3 and CH_2's.

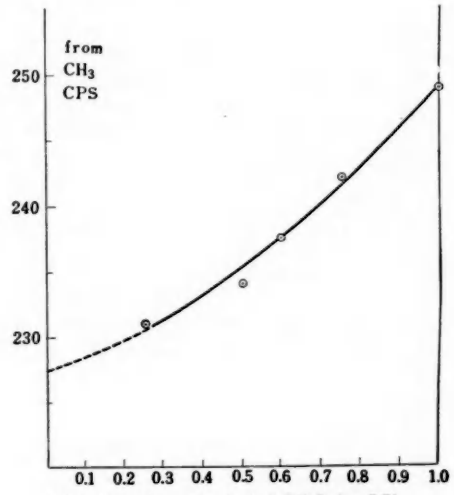

Fig. 1

In order to investigate the effects of the decomposition of the samples, the concentration dependence of the shifts were measured for the carbon tetrachloride solutions of the *n*-butylhydroperoxide.

* Presented before the 12th Annual Meeting of the Chemical Society of Japan in April, 1959.

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1) H. R. Williams and H. S. Mosher, *J. Am. Chem. Soc.*, 76, 2984 (1954).

2) These values were obtained from Fig. 6 in the article given by N. F. Chamberlain, *Anal. Chem.*, 31, 56 (1959).

The results are as shown in Fig. 1, it is seen that the OOH signal is shifted to the lower field with the increase of the concentration of the hydroperoxide, and this result will be interpreted in terms of the destruction of the structures of associated molecules as in the cases of other hydrogen-bonded liquids[3,4]. The susceptibility corrections are not made in the results of Fig. 1. Since the concentration dependence is so large that the results of the measurements with one another shifts are to be compared to each other at the same conditions of concentration. As the hydroperoxides are unstable and, moreover, it is rather difficult to determine their concentrations, we made the measurements immediately after the preparation of the samples. Hence, the results of Fig. 1 are assumed to refer to those for the actually pure hydroperoxides which are not so much different from one another in the concentration. It is also noted that α-CH_2 protons in all the samples fall in almost same position of about 79 ($\pm$1) cps. away from CH_3. Since the α-CH_2 protons in alcohols with the same carbon number as the samples showed the value of 65 ($\pm$2) cps., we notice that α-CH_2 protons in hydroperoxides are less shielded than those in alcohols as well as OOH protons. In comparison with aliphatic acids, the COOH protons which are expected to be away from CH_3 by about 275~230 cps.[2] are, as noted above, very close to the OOH protons in hydroperoxides, while α-CH_2 protons in acids are only 35 cps.[2] away from CH_3 and more shielded than those in hydroperoxides and in alcohols. Therefore, it is a quite interesting problem to investigate the chemical characters of alcohols, hydroperoxides and acids from the viewpoint of structures and of electronic distributions of OH, OOH and COOH groups.

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3) J. T. Arnold and M. E. Packard, *J. Chem. Phys.*, **19**, 1608 (1951).
4) L. W. Leeves and W. G. Schneider, *Trans. Faraday Soc.*, **54**, 314 (1958).